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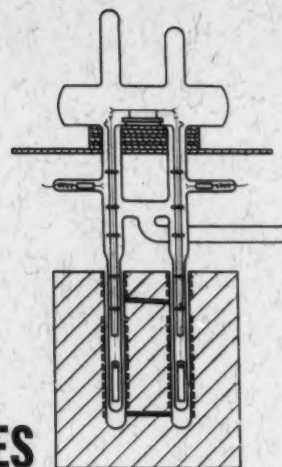
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VOLUME I

VACUUM MICROBALANCE TECHNIQUES



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Introduction by
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The proceedings of this conference provide an authoritative introduction to the rapidly widening scope of microbalance methods which is not available elsewhere in a single publication.

The usefulness of microbalance techniques in the study of the properties of materials lies in their extreme sensitivity and versatility. This renders them particularly important in studies of properties of condensed systems. In addition to the historical use of microbalance techniques as a tool of microchemistry, they have, in recent years, found extensive application in the fields of metallurgy, physics, and chemistry. The uniqueness of the method results from the facility it provides in making a series of precise measurements of high sensitivity under carefully controlled conditions over a wide range of temperature and pressure.

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AN INVESTIGATION OF SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

COMMUNICATION XXI. THE TERNARY SYSTEM $\text{Cu}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$

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Unlike the peroxides of the alkali metals of the first group of the Mendeleev periodic system, those of copper are practically unknown. Most copper-containing compounds are powerful catalysts for the decomposition of hydrogen peroxide and of a number of other peroxidic compounds. Because of this it is difficult to obtain copper peroxide if hydrogen peroxide is used as the oxidizing agent.

Numerous attempts have been made to obtain peroxidic compounds of copper. Mendeleev [1], followed by Thenard [2], Krüss [3], and Moser [4], has indicated the possibility of obtaining $\text{CuO}_2 \cdot \text{H}_2\text{O}$ by treating cupric hydroxide with solutions of hydrogen peroxide at 0° . No other peroxidic compounds of copper are referred to in the literature. Brodie [5] and Krüss [3] have used sodium peroxide as oxidizing agent, and Moser [4] used ozone. These methods, however, did not yield copper peroxide in the anhydrous state: the dehydration of the compound $\text{CuO}_2 \cdot \text{H}_2\text{O}$ resulted in its decomposition, and the dry product contained only a small quantity of active oxygen. The instability of hydrated compound may in some degree be explained if it is considered not merely as the monohydrate of copper peroxide, but also as the compound $\text{Cu}(\text{OOH})\text{OH}$; that is, cupric hydroxide in which one hydroxyl group has been replaced by one perhydroxyl group, $-\text{OOH}$.

The present work is devoted to a study of the formation of peroxidic copper compounds by treating active cupric hydroxide (the so-called "blue" hydroxide) with hydrogen peroxide solutions up to the highest attainable concentrations, within a wide temperature range from -36° to $+20^\circ$.

EXPERIMENTAL

The starting materials were hydrogen peroxide of various concentrations carefully purified from stabilizing additives by vacuum distillation, and chemically pure cupric hydroxide freshly precipitated from copper sulfate pentahydrate. The cupric hydroxide was precipitated from solutions of the sulfate by means of sodium hydroxide free from carbonate in the presence of glycerol, followed by washing with distilled water. The blue cupric hydroxide obtained was stored in darkness. Cupric hydroxide of green color was not employed, in view of its high catalytic activity towards hydrogen peroxide solutions. The investigation was performed by the ordinary methods of solubility determination at -36° , -20° , 0° and 20° , the results of chemical analysis of samples of liquid phase and solid deposit being plotted on a Gibbs triangular diagram with apices CuO , H_2O and $\frac{1}{2}\text{O}_2^{\text{act}}$ (active oxygen).

The active oxygen content was determined by titration with 0.1N potassium permanganate in acid solution in the presence of boric acid. The cupric oxide was determined in the form of metallic copper by electrolysis in sulfuric acid solution after removal of active oxygen. The content of dissolved copper in the liquid phase was negligibly small, of the order of $10^{-4}\%$. Additional experiments were carried out to determine the copper content in the liquid phase, calculated as cupric oxide. These were performed by an electrophotocolorimeter of type FEK-M, using the compound with dithiazone at pH 2, using a yellow light filter transparent around 510 mμ.

Under the conditions employed, the interaction of hydrogen peroxide with cupric hydroxide took place rapidly, and it could be reckoned that equilibrium was practically completely established within 10-15 minutes, after which appreciable decomposition of the solid phase formed commenced. This decomposition took place more rapidly the higher the temperature used.

Data obtained on the solubility isotherms in the system $\text{Cu}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$.

Isotherm for -36° . The study of equilibria at -36° was carried out from the limit of crystallization of ice from 40.75 to 73.20% in the liquid phase (Table 1).

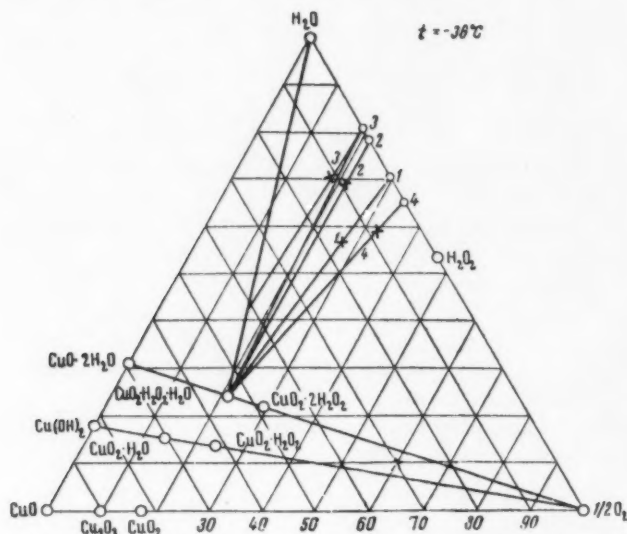


Fig.1. Isotherm for -36° for the ternary system $\text{Cu}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$.

Figure 1 presents, in the form of a Gibbs triangular diagram, the directions of the residue composition lines, and gives a visual demonstration of the fact that, within the hydrogen peroxide concentration limits studied at -36° in the liquid phase, the only solid phase equilibrium involves the appearance of a new, formerly unknown compound of formula $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

TABLE 1.

Comp. of liquid phase, wt. %			Comp. of residue, wt. %			Solid phases
active O_2	H_2O_2	H_2O	active O_2	CuO	H_2O	
19,15	40,75	80,85	18,98	10,44	70,58	Ice + $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
21,61	45,92	78,39	22,05	8,96	68,99	
29,02	61,73	70,93	26,40	16,71	56,89	The same » »
33,04	70,00	66,94	—	—	—	
35,45	73,20	65,55	32,38	8,41	59,21	

Isotherm for -20° . The investigation carried out at -20° was for study of liquid phase concentrations of hydrogen peroxide from 24.45 to 81.39% (Table 2).

The diagram for this isotherm (Fig.2) shows that at -20° , in addition to the phase $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ established for -36° , there also exists a solid phase of composition corresponding to $\text{CuO}_2 \cdot \text{H}_2\text{O}$, which has been described earlier in the literature. This monohydrate of copper peroxide exists in equilibrium with aqueous hydrogen peroxide within the hydrogen peroxide concentrations 24.45-43.05%: that is, just at the concentrations characteristic of ordinary "perhydrol." At concentrations in the liquid phase higher than 43.05% hydrogen peroxide, the solid phase $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ is formed, with a higher active oxygen content.

Isotherm for 0° . At this temperature the hydrogen peroxide concentrations studied were from 0 to 86.87% in the liquid phase. The facts obtained are shown in Table 3, and in diagrammatic form in Fig.3. They show that three solid phases may exist at this temperature: cupric hydroxide up to 4.33% hydrogen peroxide in the liquid phase; $\text{CuO}_2 \cdot \text{H}_2\text{O}$ from 4.33 to 40.51%; and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ at higher values. The nature of the peroxidic phases is thus unchanged compared with -20° .

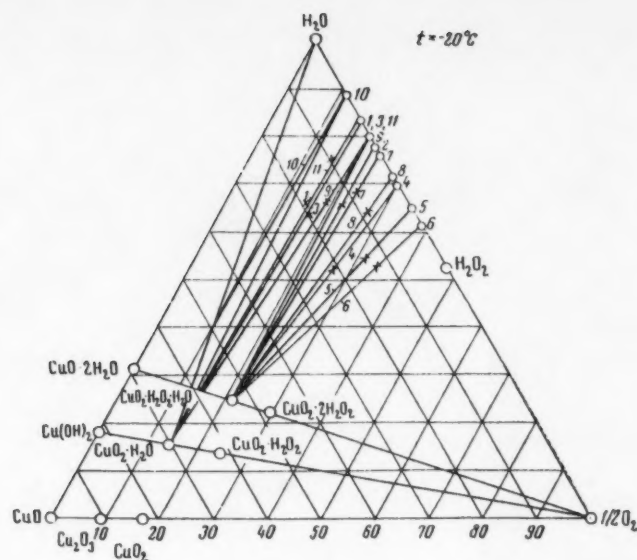


Fig. 2. Isotherm for -20° for the ternary system $\text{Cu}(\text{OH})_2\text{--H}_2\text{O}_2\text{--H}_2\text{O}$.

TABLE 2.

Comp. of liquid phase, wt. %			Comp. of residue, wt. %			Solid phases
active O_2	H_2O_2	H_2O	active O_2	CuO	H_2O	
11,51	24,45	88,49	11,32	9,96	78,72	Ice + $\text{CuO}_2 \cdot \text{H}_2\text{O}$ $\text{CuO}_2 \cdot \text{H}_2\text{O}$ The same
16,45	34,95	83,51	16,31	20,25	63,44	
16,46	34,97	83,49	16,00	18,66	65,34	
17,11	36,36	82,89	16,90	10,55	72,55	$\text{CuO}_2 \cdot \text{H}_2\text{O} + \text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ The same
20,26	43,05	79,74	19,53	11,81	68,66	
22,70	48,24	77,30	21,51	21,83	56,66	
23,80	50,57	76,20	22,92	9,50	67,58	» » » » »
28,75	61,09	71,25	27,44	8,91	63,65	
30,00	63,72	69,97	27,14	21,88	50,98	
34,93	74,22	65,03	31,16	14,80	54,04	
38,30	81,39	61,67	34,16	12,95	52,89	

Isotherm for 20° . At this temperature, concentrations of hydrogen peroxide up to 82,96% were used. The data are given in Table 4 and presented graphically in Fig. 4. It is seen from this that the solid phases remain the same at this temperature: up to 0,51% hydrogen peroxide the solid phase is cupric hydroxide; from this value to 54,61% it consists of $\text{CuO}_2 \cdot \text{H}_2\text{O}$, and for higher concentrations it becomes $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

The solubility of cupric hydroxide in the system $\text{Cu}(\text{OH})_2\text{--H}_2\text{O}_2\text{--H}_2\text{O}$. The limits within which the solid phases ice, cupric hydroxide, $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ can exist under isothermal conditions at -36° , -20° , 0° , and 20° , found by the method of residues, can be established sufficiently well without taking account of the solubility of cupric hydroxide in the liquid phase. But in view of the great interest attaching to the change it was decided to carry out a systematic study with a view to constructing the complete solubility isotherms for 0° and -20° .

The data obtained at 0° and -20° , recalculated in terms of cupric oxide, are given in Tables 5 and 6, and represented graphically in Figs. 5 and 6.

Thus, at 0° , the solubility of $0,23 \times 10^{-4}\%$ exhibited by the oxide in water increases, characteristically, at a rapid rate, reaching about $12,0 \times 10^{-4}\%$ for the simultaneous existence of solid phases $\text{Cu}(\text{OH})_2$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}$; and about $9,51 \times 10^{-4}\%$ for the simultaneous existence of $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$.

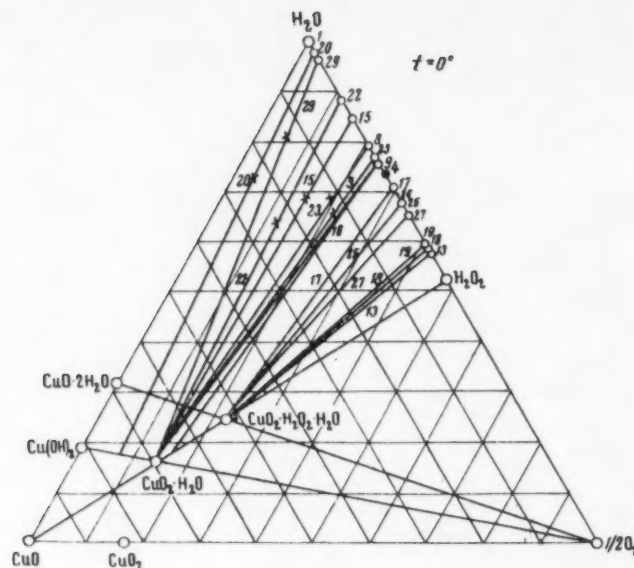


Fig.3. Isotherm for 0° for the ternary system $\text{Cu}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$.

TABLE 3.

Comp. of liquid phase, wt. %			Comp. of residue, wt. %			Solid phases
active O_2	H_2O_2	H_2O	active O_2	CuO	H_2O	
2,04	4,33	97,96	4,00	20,15	75,85	$\text{Cu}(\text{OH})_2 + \text{CuO}_2 \cdot \text{H}_2\text{O}$
3,82	8,11	96,18	5,31	11,88	82,81	$\text{CuO}_2 \cdot \text{H}_2\text{O}$
11,88	25,25	88,12	11,91	26,06	62,03	The same
15,55	33,04	84,45	14,50	16,72	68,78	"
20,87	44,35	79,13	19,17	12,70	68,13	"
22,78	48,41	77,22	21,21	13,99	64,80	"
23,77	50,51	76,23	21,49	17,40	61,11	$\text{CuO}_2 \cdot \text{H}_2\text{O} + \text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
29,52	62,73	70,48	26,36	15,56	58,08	$\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
30,01	63,77	70,00	24,60*	19,12	56,28	The same
32,06	68,05	67,94	27,16	22,77	50,07	"
34,60	73,52	65,40	28,47	21,75	49,78	"
40,31	85,66	59,69	35,47	13,72	50,81	"
40,67	86,42	59,33	35,01	15,76	49,23	"
41,68	88,57	58,32	37,06	11,68	51,26	"

* The active oxygen content was reduced because of partial decomposition.

A similar picture is also observed for the solubility diagram at -20° . A maximum of $8,76 \times 10^{-4}\%$ is found for the simultaneous existence of $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. Such an increase in the solubility of the hydroxide is apparently characteristic for systems consisting of water, hydrogen peroxide, and the slightly soluble hydroxides of elements of the subsidiary subgroups: copper, zinc etc.

The diagrams obtained for the solubility isotherms at 0° and -20° thus confirm the completeness of the diagram arrangement described in the first part of this work.

Polytherms for the system $\text{Cu}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$. The experimental information obtained permits us to establish the temperature and concentration limits for the existence of the ternary solid phase system: ice, $\text{Cu}(\text{OH})_2$, $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. Owing to the very low solubility of cupric hydroxide (or oxide) in the liquid phase, the space polythermal diagram may practically be projected onto a plane on the axes t° - % hydrogen peroxide (Fig.7). The lines on this diagram defining the limits for the crystallization of ice and solid hydrogen peroxide are taken from the well-

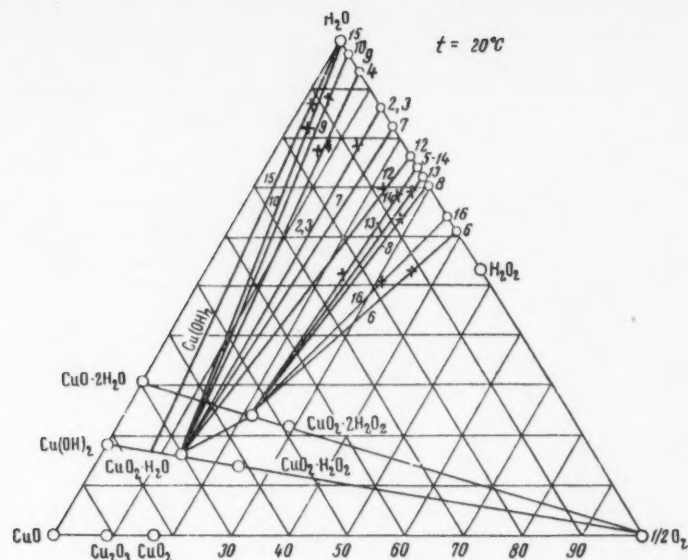


Fig.4. Isotherm for 20° for the ternary system $\text{Cu(OH)}_2\text{-H}_2\text{O}_2\text{-H}_2\text{O}$.

TABLE 4.

Comp. of liquid phase, wt. %			Comp. of residue, wt. %			Solid phases
active O_2	H_2O_2	H_2O	active O_2	CuO	H_2O	
0,24	0,51	99,76	2,20	12,58	85,22	$\text{Cu(OH)}_2 + \text{CuO}_2 \cdot \text{H}_2\text{O}$
1,74	3,70	98,26	3,00	12,47	84,53	$\text{CuO}_2 \cdot \text{H}_2\text{O}$
2,78	5,91	97,22	3,87	8,42	87,71	The same
6,60	14,02	93,40	7,12	16,12	76,76	"
14,06	29,80	85,94	13,29	16,10	70,61	"
14,06	29,88	85,95	13,19	16,20	70,61	"
17,70	37,61	82,30	16,79	9,06	74,15	"
23,45	49,61	76,55	22,10	8,86	69,04	"
25,70	54,61	74,30	24,84	8,67	66,49	$\text{CuO}_2 \cdot \text{H}_2\text{O} + \text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
26,40	56,10	73,60	23,84	25,00	51,15	$\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
28,54	60,65	71,46	26,67	9,26	64,07	The same
29,69	63,09	70,31	38,37	7,67	53,95	"
35,50	75,44	64,50	31,65	18,25	50,10	"
39,04	82,96	60,96	35,02	11,80	53,18	"

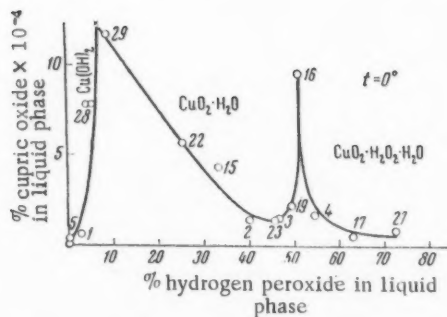


Fig.5. Solubility of cupric oxide at 0° and -20°.

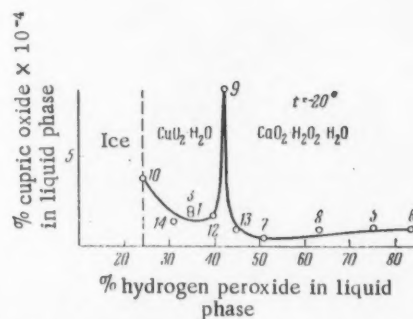


Fig.6. Solubility of cupric oxide at -20° in aqueous hydrogen peroxide.

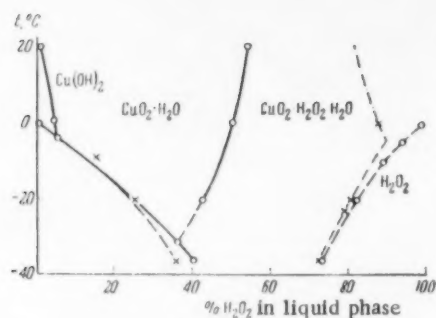


Fig. 7. Concentration limits for the existence of solid phases in the system $\text{Cu}(\text{OH})_2\text{-H}_2\text{O}_2\text{-H}_2\text{O}$.

TABLE 5.

Comp. of liquid phase, wt. %				Solid phases
active O_2	H_2O_2	$\text{X} \cdot 10^{-4}$ CuO	H_2O	
0,0	0,0	0,23	100	$\text{Cu}(\text{OH})_2$
1,16	2,47	0,55	93,84	The same
2,27	4,82	7,77	97,73	»
2,04	4,33	~12,0	97,96	$\text{Cu}(\text{OH})_2 + \text{CuO}_2 \cdot \text{H}_2\text{O}$
3,89	8,26	11,6	96,11	$\text{CuO}_2 \cdot \text{H}_2\text{O}$
12,12	25,75	5,65	87,88	The same
15,77	33,51	4,4	84,23	»
19,06	40,50	1,5	80,94	»
21,71	46,13	1,55	78,29	»
21,96	46,66	1,5	78,04	»
23,30	49,51	2,25	76,70	»
23,80	50,57	9,51	76,20	$\text{CuO}_2 \cdot \text{H}_2\text{O} + \text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
26,21	55,10	1,79	73,79	$\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
29,97	63,68	0,59	70,03	The same
34,13	72,52	0,85	65,87	»

TABLE 6.

Composition of liquid phase, wt. %				Composition of residue, weight, %				Solid phases
$\text{X} \cdot 10^{-4}$ CuO	act. O_2	H_2O_2	H_2O	CuO	act. O_2	H_2O_2	H_2O	
3,88	11,5	24,4	75,6	12,40	11,72	—	75,88	$\text{Ice} + \text{CuO}_2 \cdot \text{H}_2\text{O}$
1,35	14,84	31,54	68,46	—	—	—	—	$\text{CuO}_2 \cdot \text{H}_2\text{O}$
2,00	16,2	34,4	65,6	13,48	16,25	—	70,27	The same
1,9	16,2	34,4	65,6	—	—	—	—	»
1,68	18,89	40,14	59,86	—	—	—	—	»
8,76	19,4	42,3	57,7	11,9	19,45	—	68,65	$\text{CuO}_2 \cdot \text{H}_2\text{O} + \text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
1,03	20,96	44,54	55,46	—	—	—	—	$\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$
0,51	24,0	51,1	48,9	11,9	22,83	—	65,27	The same
0,80	24,8	63,3	36,7	9,51	28,21	—	62,28	»
1,05	35,4	75,1	24,9	10,08	32,57	—	57,35	»
1,04	39,6	84,1	15,9	5,40	40,90	—	54,70	$\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}_2$

known data for the water-hydrogen peroxide system [6]. A considerable section of the diagram is occupied by two regions for the existence of solid phases of the peroxide type, $\text{CuO}_2 \cdot \text{H}_2\text{O}$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$. The concentration limits with respect to hydrogen peroxide for the existence of $\text{CuO}_2 \cdot \text{H}_2\text{O}$ in equilibrium with the liquid phase show a tendency to widen with rise in temperature, while those for $\text{Cu}(\text{OH})_2$ and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, on the other hand, diminish. In regions of high hydrogen peroxide concentration, the limit of investigation is determined by the stability of the hydrogen peroxide solutions.

SUMMARY

1. The system $\text{Cu}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ has been studied by a solubility method at temperatures of -36° , -20° , 0° and 20° .
2. In addition to the peroxidic compound of copper formerly known, $\text{CuO}_2 \cdot \text{H}_2\text{O}$, the existence of a new compound with a higher content of active oxygen, $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ has been established, this being formed at higher concentrations of hydrogen peroxide in the liquid phase.
3. A polythermal diagram constructed for the temperature range -36° to $+20^\circ$, giving the limits of equilibrium existence of the solid phases ice, cupric hydroxide, $\text{CuO}_2 \cdot \text{H}_2\text{O}$, and $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, has been obtained.
4. The solid phases of peroxide type obtained have been submitted to additional thermal studies. The compound $\text{CuO}_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$ has served as a basis for the synthesis of anhydrous cupric peroxide, CuO_2 .

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THE KINETICS AND MECHANISM OF THE INTERACTION OF METHYL RADICALS WITH MOLECULAR OXYGEN

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The kinetics of the reaction between methyl radicals and molecular oxygen have been little studied up to the present. Only the work of Hoare and Walsch [1] has been devoted to determining the rate constant of this reaction. Considerably more attention has been given to the mechanism of this reaction, which was first considered in the work of Bates and Spence [2]. Recently a group of investigators [3-9] have carried out investigations of this reaction. A critical review of the work of previous authors has led us to the conclusion that it remains necessary to provide an explanation of certain details of the mechanism of this reaction. In particular, the appearance of the primary and secondary products of the reaction, the measurement of the kinetics (rate constants) of the elementary stages, and the development of side products, seem to us to be most important problems still awaiting solution. One of the most important questions as to the mechanism of the reactions concerns the formation of formaldehyde. This problem is still in dispute, since certain authors [4,9] believe that the peroxidic radical CH_3OO leads to the formation of the formaldehyde, while others [1,5] question this.

EXPERIMENTAL

In order to resolve these questions, an apparatus was constructed with which the experiments could be carried out under more refined conditions than had been used by other authors. In our experiments, side reactions (the effect of light in producing photochemical reactions), and also quadratic reactions, could be excluded. The plan of the apparatus is shown in Fig.1. The principal characteristic of the apparatus was that the source of the methyl radicals (the place where thermal dissociation of acetone was brought about) was separated by a jet from the zone of reaction between the methyl radicals and oxygen. The apparatus includes a quartz reaction vessel 3, fused to another quartz tube 1 in which the pyrolysis of acetone occurs, the products of this passing through the jet 2 into the reactor. Acetone vapor is introduced at a constant rate into the pyrolysis zone from the thermostated vessel 11. The products of pyrolysis, containing methyl radicals, pass together with acetone through the jet into the reactor, where they mix with the oxygen introduced through one of the leads 5-8. The oxygen enters at a constant rate from the calibrated flask 12 through the tap valve 13. The reaction products are condensed in a detachable trap 9, and subsequently submitted to analysis. The pressure in the reactor is measured by means of the mercury manometer, is used reading microscope, to an accuracy of 0.1 mm Hg.

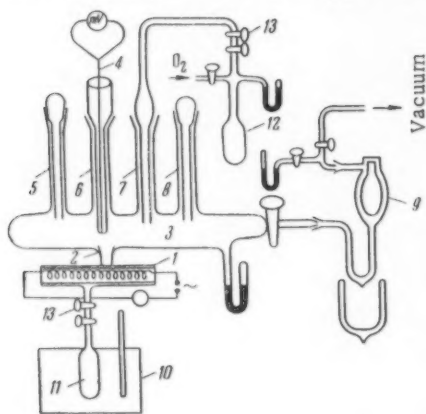
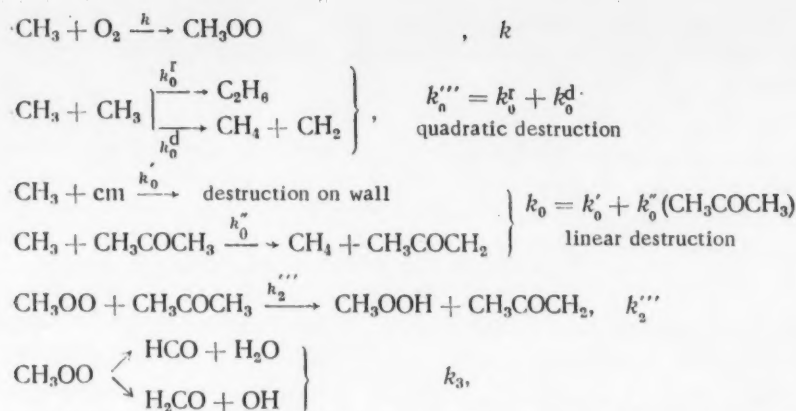


Fig. 1. Scheme of apparatus: 1) Tube for pyrolysis of acetone; 2) jet; 3) reactor; 4) thermocouple; 5-8) leads for addition of O_2 ; 9) detachable trap; 10) thermostat; 11) vessel with acetone; 12) calibrated flask; 13) tap valve.

Together with the qualitative study of the course of the reaction in this apparatus, it was possible to measure the rate constants of the primary elementary reactions. For this purpose we used a method developed by us [10] for determining the rate constants of reactions of atoms and radicals. According to this method, by measuring the constant for the production of methyl peroxide it was possible to determine the effective rate constant for the interaction of radicals and molecular oxygen, on the basis of the accepted mechanism. The mechanism used for this purpose for the over-all course of the reaction is shown in the following scheme:



where k is the effective rate constant for the formation of the peroxidic radical; k_0^r is the rate constant for the recombination of methyl radicals; k_0^d is the rate constant for the disproportionation of methyl radicals; k_0''' is the total constant for the rate of quadratic destruction of methyl radicals; k_0 is the total constant for the rate of linear destruction of methyl radicals; k_2''' is the rate constant for the formation of methyl peroxide; and k_3 is the rate constant for the unimolecular decomposition of the peroxidic radical.

On the basis of this mechanism, according to the method described earlier [10] for the case of the bimolecular reaction between methyl radicals and molecular oxygen, the equation obtained is:

$$\frac{1}{(\text{CH}_3\text{OOH})_k} = \frac{a}{(\text{CH}_3)_0} + \frac{[k_0 + k_0'''(\text{CH}_3)_0] a}{k_1(\text{O}_2)_0(\text{CH}_3)_0}, \quad (1)$$

where k_1 is the rate constant for the bimolecular interaction of the methyl reaction with molecules of oxygen; $(\text{CH}_3\text{OOH})_k$ is the final concentration of methyl perhydroxide; $(\text{CH}_3)_0$ is the initial concentration of the methyl radical; $(\text{O}_2)_0$ is the initial concentration of molecular oxygen; and $1/a$ is the fraction of the initial concentration of methyl radical taking part in the formation of the peroxidic radical. For the termolecular mechanism for the formation of the peroxidic radical, the equation obtained is:

$$\frac{1}{(\text{CH}_3\text{OOH})_k} = \frac{a}{(\text{CH}_3)_0} + \frac{[k_0 + k_0'''(\text{CH}_3)_0] a}{k_2(M)(\text{O}_2)_0(\text{CH}_3)_0}, \quad (2)$$

where k_2 is the rate constant of the termolecular reaction; (M) is the concentration of the third particle. When the mechanism of the formation of the peroxidic radical involves both binary and ternary processes, the equation obtained is:

$$\frac{1}{(\text{CH}_3\text{OOH})_k} = \frac{a}{(\text{CH}_3)_0} + \frac{[k_0 + k_0'''(\text{CH}_3)_0] a}{[k_1 + k_2(M)](\text{O}_2)_0(\text{CH}_3)_0}. \quad (3)$$

Equations (1) and (3) are equations of straight lines, from which, by measuring the magnitude $(\text{CH}_3\text{OOH})_k$ in relation to that of $(\text{O}_2)_0$ (for constant temperature, pressure, and methyl radical initial concentration), the magnitude $k_1 + k_2(M)$ may be obtained if that of the sum $k_0 + k_0'''$ is known.

Thus it is easy to see that, in the general case, the effective rate constant of the reaction is determined as:

$$k = k_1 + k_2(M). \quad (4)$$

The effective magnitude of the total destruction of the methyl radical, $k_0 + k_0'''(\text{CH}_3)_0$ is determined by the method described earlier [11] for the ethyl radical. Accepting the reasoning set out in the previous article [11] for determining the over-all destruction of ethyl radicals under the flow conditions of the experiment, under circumstances under which quadratic destruction of the methyl radical is predominant, we obtain the equation:

$$\frac{(\text{CH}_3)_0}{(\text{CH}_3)_x} = 1 + \left[\frac{k_0 + k_0'''(\text{CH}_3)_0}{w} \right] \cdot x, \quad (5)$$

where $(\text{CH}_3)_x$ is the concentration of methyl radicals in the reaction vessel at distance X cm from the jet; w is the linear velocity of the stream; and X is the distance from the jet to the place at which the change* in the concentration of the methyl radicals occurs.

Measurement of the relative concentrations $(\text{CH}_3)_0/(\text{CH}_3)_x$ of the methyl radical for various distances X , according to the limiting rates of development of hydroperoxide, the magnitude of the over-all destruction, $k_0 + k_0''(\text{CH}_3)_0$, may be obtained from the tangent of the slope of the straight line given by equation (5). The product of the tangent of the slope and the linear velocity of the stream gives the total rate required. The correctness of measuring the relative concentrations of methyl radicals from the ratio of the limiting rates of development of methyl perhydroxide follows from the proportionality between the limiting rate of this process and the concentration of the methyl radical. Thus, in order to determine the magnitude of k by our method it is necessary to determine the relationship between the yield of the perhydroxide and the concentration of molecular oxygen introduced initially through one of the leads, and then the limiting yields of hydroperoxide when the oxygen is introduced through other leads.

In cases for which the experimental data satisfy equation (5), and for which the quadratic destruction predominates over the linear, it becomes possible to determine the rate constant for quadratic destruction, k_0'' . For this purpose it is necessary, also, to determine the initial concentration of the methyl radical, $(\text{CH}_3)_0$. This may be done in different ways, and in particular by using the intercept $b = a/(\text{CH}_3)_0$ of the straight line of equation (3) on the axis of ordinates. This requires in turn the determination of the magnitude of a . Using the postulated reaction scheme we then obtain:

$$a = 1 + \frac{k_3}{k_2''(\text{CH}_3\text{COCH}_3)} \quad (6)$$

The equation then obtained for b is therefore:

$$b = \frac{1}{(\text{CH}_3)_0} + \frac{k_3}{k_2''(\text{CH}_3\text{COCH}_3)} \quad (7)$$

This is also the equation of a straight line relationship between the variables b and $(\text{CH}_3\text{COCH}_3)$. When the line is constructed on the basis of the experimental points, it is not difficult to obtain both the magnitude of $(\text{CH}_3)_0$ and the ratio of the constants k_3/k_2'' .

In the particular case for which the rate of decomposition of the peroxidic radical CH_3OO , characterized by the constant k_3 , is less than the rate of formation of methyl perhydroxide, characterized by the quantity $k_2''(\text{CH}_3\text{COCH}_3)$; that is when:

$$\frac{k_3}{k_2''(\text{CH}_3\text{COCH}_3)} < 1;$$

we obtain from (6) that $a \sim 1$, and from (7) that:

$$b \sim \frac{1}{(\text{CH}_3)_0}$$

Discussion of Experimental Results

It is first necessary to reveal the main course of the reaction. Among the probable reaction products according to the over-all proposed mechanism might be expected: methyl perhydroxide, formaldehyde, and oxides of carbon. Experimentally discovered were: the perhydroxide and carbon dioxide. Methyl perhydroxide was determined quantitatively by two methods: titration of the condensate obtained by the iodometric method in acid solution, and by a polarographic procedure. For identification of methyl perhydroxide by the polarographic method, and for graduation of the polarograph, methyl perhydroxide was synthesized using the method of [12]. Whether formaldehyde was present was investigated qualitatively by means of the very sensitive Rimini reaction (using phenylhydrazine hydrochloride + potassium ferrocyanide + hydrochloric acid). Carbon dioxide was determined by titration in acetone solution using thymol blue as indicator.

The results showed that the principal oxygen-containing reaction product was methyl perhydroxide. Not even traces of formaldehyde were found. Since it might be expected that formaldehyde would appear at a higher temperature, search was made for it in the temperature range 100-450°. No traces were found at these temperatures either.

*So the Russian text. But the next paragraph makes it likely that "izmerenie" (measurement) is intended instead of "izmenie" (change) [Publisher's note].

The carbon dioxide discovered represented about 30% of the quantity of perhydroxide. Carbon dioxide was thus not the principal reaction product, and originates, apparently, from a secondary process. The carbon monoxide was not determined, since it originated mainly from the thermal decomposition of the acetone.

It was shown by numerous measurements that, over a wide range of temperature and flow rate, the relationship between the production of perhydroxide and the addition of molecular oxygen into the reaction zone is described by a curve characteristic for the primary product [13] with saturation. Figure 2 gives a shortened curve of this kind, obtained at 100° and total pressure $P_{\text{tot}} = 0.6$ mm Hg.

Figure 3 gives the value of $a/(\text{CH}_3)_0 = 7.8 \times 10^{-13}$ from the intercept on the axis of ordinates, and from the tangent of the angle of inclination of the straight line gives the value of the ratio:

$$\frac{k}{k_0 + k_0''(\text{CH}_3)_0} = 2.63 \cdot 10^{-13}.$$

To calculate the absolute values of the rate constant k , it is necessary to determine the value of the sum: $k_0 + k_0''(\text{CH}_3)_0$. This sum is obtained from the line described by equation (5), giving the relationship between the relative concentrations of the methyl radicals and the distance from the jet. This relationship is shown on Fig. 4, obtained from the data of Fig. 2. The relative concentration of the methyl radicals $(\text{CH}_3)_0/(\text{CH}_3)_x$ was determined from the limiting rate of formation of the perhydroxide at different distances from the jet. Figure 4 gives the value of $k_0 + k_0''(\text{CH}_3)_0$ as 46.7 sec⁻¹. The maximum error in this sum is estimated at 35%. The linear velocity of the stream in these experiments was $w = 550$ cm/sec.

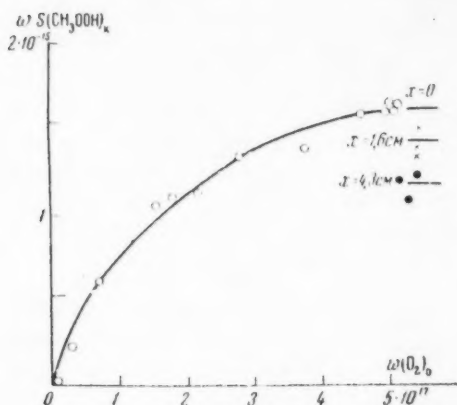


Fig. 2. Relationship between the rate of production of methyl perhydroxide and the current velocity, $w(\text{O}_2)_0$, of molecular oxygen: 1) Curve for introduction of oxygen to the jet at distance of 0 cm from the jet; 2) shift of curve when oxygen is added at distance of 1.6 cm from the jet; 3) shift of the curve when oxygen is added at distance 4.3 cm from the jet.

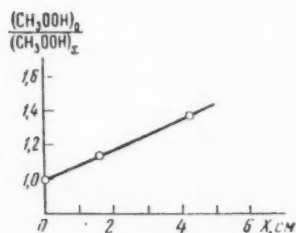


Fig. 4. Relationship between relative concentrations of the methyl radical and distance from the jet.

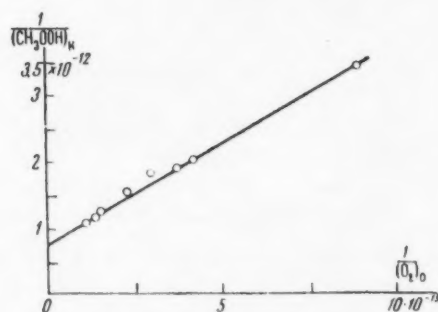


Fig. 3. Relationship between $1/(\text{CH}_3\text{OOH})_x$ and the reciprocal of the initial concentration of molecular oxygen.

It follows that the value of $k = 1.23 \times 10^{-13}$ cm³sec⁻¹. The values obtained also permit estimation of the absolute value of the rate constant for quadratic destruction of methyl radicals, k_0'' . Figure 4 shows that the experimental points lie well on a straight line, while this, according to the description already given [11], is evidence of the prominence of quadratic destruction over linear. Hence, without great error, the value is obtained: $k_0''(\text{CH}_3)_0 = 46.6$ sec⁻¹. It is shown by this, that, for the determination of the value of k_0'' it is necessary to know the initial concentration of methyl radicals, $(\text{CH}_3)_0$. From Fig. 3 we have already obtained the value:

$$b = \frac{a}{(\text{CH}_3)_0} = 7.8 \cdot 10^{-13} \text{ cm}^3.$$

If we accept a minimum value for the quantity a , equal to unity, then Fig. 3 gives a minimum value for $(\text{CH}_3)_0$. We thus obtain $(\text{CH}_3)_0 \geq 1.28 \times 10^{12}$. Hence:

$$k_0'' = \frac{46.7}{(\text{CH}_3)_0} \quad \text{or: } k_0'' \leq 3.65 \times 10^{-11} \text{ cm}^3 \text{sec}^{-1} \text{mol}^{-1}.$$

TABLE 1.

Temp., °K	Pressure p, mm Hg	Molecule of third fraction	k_0'''	Refer- ence
400-450	10-50	CH ₃ COCH ₃	$7,4 \cdot 10^{-11}$	[14]
600	0,2	Hg(CH ₃) ₂	$1,8 \cdot 10^{-12}$	[15]
1125	15,5	[(CH ₃) ₃ CO] ₂	$0,67-1,14 \cdot 10^{-11}$	[16]
438	10	Helium	$6,1 \cdot 10^{-11}$	[17]
434	9	CH ₃ COCH ₃	$2,34 \cdot 10^{-11}$	[18]
	0,2-20	Helium	$2 \cdot 10^{-11}$	[19]
		CH ₃ COCH ₃	$6 \cdot 10^{-11}$	[20]

The results obtained in calculating the value of k_0''' are in satisfactory agreement with the data of other authors set out in Table 1.

TABLE 2.

Temp., °K	$k_0 + k_0'''$ (CH ₃) ₂ O	$a/(CH_3)_0$	$k, \text{cm}^3 \cdot \text{sec}^{-1}$
373	46,7	$7,8 \cdot 10^{-13}$	$1,2 \cdot 10^{-13}$
473	62,2	$9,1 \cdot 10^{-13}$	$1,3 \cdot 10^{-13}$
573	70,5	$6,1 \cdot 10^{-13}$	$1,8 \cdot 10^{-13}$

The results of these experiments have shown, within the limits of experimental error, that pressure variation has no effect on the value of k . At pressures of 3 and 3.5 mm the constant k was found to be equal to $0,9 \times 10^{-13} \text{ cm}^3 \cdot \text{sec}^{-1}$. In the work of Hoare and Walsch [1] some effect of the third constituent on the value of k was observed in the pressure range 10-200 mm Hg, though it was noted that this effect was less marked at 10 mm than at pressures between 30 and 200 mm. These authors explained the reduction of the effect of pressure on the value of k on the assumption that the importance of the bimolecular reaction $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{OO} \cdot$ increased at low pressures.

Figure 5 shows the relationship between k and the acetone pressure over a wide pressure range. The crosses denote the values found in the experiments of Hoare and Walsch; the points denote values obtained by ourselves, and the open circles denote values obtained by Marcotte and Noyes [3]. The figure shows that it is possible to construct a straight line through all the points obtained by the various authors, the line giving an intercept on the axis of ordinates.

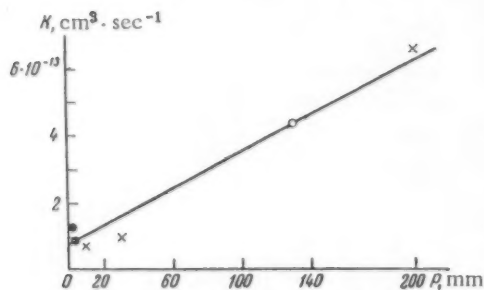


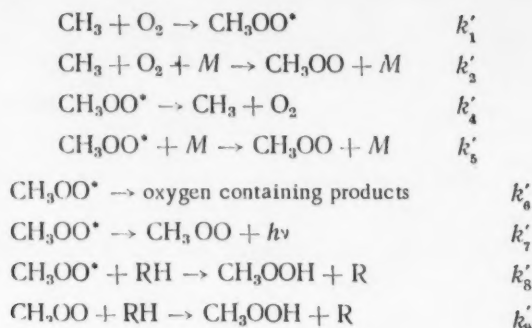
Fig.5. Relationship between the effective rate constant of the reaction between the methyl radical and molecular oxygen and the acetone pressure.

Experiments have also been carried out at 200° and 300°. Curves have obtained in these series of experiments similar to those shown in Figs.2-4. The results of experiments at different temperatures, at a common pressure of 0.6 mm Hg are shown in Table 2. The maximum error in the value of k is estimated at 50%.

Table 2 shows that the reaction between the methyl radical and oxygen proceeds with practically zero activation energy. To elucidate the problem of the effect of a third constituent on the size of the effective constant k , measurements of k were carried out at acetone pressures of 0.6, 3.0 and 3.5 mm Hg.

Having regard to the wide range of the experimental points, it may be taken that the straight line satisfactorily includes them all. It is clear from Fig.5 that the straight line does not pass through the origin, but has a certain intercept on the axis of ordinates. It might well have been thought that it did pass through the origin, but for our measurements carried out at low pressures on the value of k , but in view of these this is not possible. Thus, a combination of the experimental results of several authors establishes the law governing the effect of the third constituent (acetone) on the effective rate constant for the reaction between the methyl radical and molecular oxygen. This law is, in the general case, described by equation (4). By the use of Fig.5 it is possible to determine both the bimolecular constant k_1 , and the termolecular k_2 . This way of treating the experimental results, however, does not reveal the full structure of the constants k_1 and k_2 : It merely shows that they are the bimolecular and termolecular constants, respectively. But which actual elementary reactions are depicted by these constants is not clear.

To elucidate these actual elementary reactions depicted by the constants k_1 and k_2 and k , we consider the partial scheme for the mechanism of the interaction between methyl radicals and molecular oxygen, leading to the formation of the peroxidic radical:



Using the stationary condition, $d(\text{CH}_3\text{OO}^*)/dt = 0$, and employing certain rearrangements sufficiently described earlier [21], we obtain the structure of the effective constant form:

$$k = k'_2(M) + \frac{k'_1[k'_6 + k'_7 + k'_8(\text{RH}) + k'_9(M)]}{k'_4 + k'_6 + k'_7 + k'_8(\text{RH}) + k'_9(M)} \quad (8)$$

Equation (8) may be represented graphically in a way similar to that described earlier [21], either as a saturation curve, or as a straight line. The saturation curve is only obtained when the second component of equation (8) predominates over the first, but the straight line may be obtained in both cases. Firstly, when the first component of equation is the dominant one, we have the conditions:

$$k'_2(M) \gg \frac{k'_1[k'_6 + k'_7 + k'_8(\text{RH}) + k'_9(M)]}{k'_4 + k'_6 + k'_7 + k'_8(\text{RH}) + k'_9(M)} \quad (9)$$

while, when the second term is dominant, and has attained to its saturation value at which it no longer depends on the pressure, we have the conditions:

$$k'_2(M) \ll k'_1 \quad (10)$$

Saturation in the curve arises when:

$$\frac{k'_1[k'_6 + k'_7 + k'_8(\text{RH}) + k'_9(M)]}{k'_4 + k'_6 + k'_7 + k'_8(\text{RH}) + k'_9(M)} = 1.$$

Since, in the experiment depicted in Fig.5, a straight line is obtained over a wide pressure range, and since this straight line gives an intercept on the axis of ordinates, it is clear that in this case the conditions of (10) are realized. Hence equation (8) may be reduced to the approximate equality:

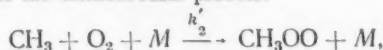
$$k = k'_2(M) + k'_1 \quad (11)$$

This equation depicts the experimental straight line of Fig.5, and is distinguished from equation (4) only by the fact that it now reveals the actual elementary acts described by the bimolecular constant k'_1 and the termolecular constant k'_2 .

The experimental straight line in Fig.5 permits the determination of the absolute value of the rate constants of the bimolecular and termolecular reactions. The value of the former, for the process $\text{CH}_3 + \text{O}_2 \xrightarrow{(k'_1)} \text{CH}_3\text{OO}^*$ is obtained from the intercept cut off by the straight line on the axis of ordinates. From Fig.5 we obtain:

$$k'_1 = 0,8 \cdot 10^{-13} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{mol}^{-1}$$

The size of the rate constant for the termolecular process:



is obtained from the tangent of the slope of the straight line as:

$$k'_2 = 1,35 \cdot 10^{-31} \text{ cm}^6 \cdot \text{sec}^{-1} \cdot \text{mol}^{-2}.$$

SUMMARY

1. The mechanism of the interaction of methyl radicals with molecular oxygen has been studied at pressures from 0.5 to 3.5 mm Hg and at temperatures from 100° to 450°.
2. The products of the reaction have been found to include methyl perhydroxide and carbon dioxide. The perhydroxide is the most important of the oxygen-containing compounds detected.
3. Formaldehyde was not detected among the reaction products in the interaction of methyl radicals and oxygen.
4. The effective rate constant of the elementary reaction of the methyl radical with molecules of oxygen has been measured.
5. The absolute value of the rate constant has been determined for the bimolecular reaction $\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{OO}^\bullet$, and for the termolecular reaction $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{OO} + \text{M}$.

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CARBON FORMATION DURING THE DECOMPOSITION
OF ISOPROPANOL, n-HEXANOL, AND CYCLOHEXANOL
ON A COPPER-SILICA-GEL CATALYST.

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Khimicheskikh Nauk, No. 11,

pp. 1930-1937, November, 1960

Original article submitted June 29, 1959

In previous works [1,2] it has been shown that during the decomposition of ethyl alcohol on a copper-silica-gel catalyst, two mechanisms for the formation of fatty and carbonaceous substances occur on increasing the temperature from 200° to 950°. The low temperature mechanism (200°-600°) consists of the polycondensation of acetaldehyde previously produced by the catalytic dehydrogenation of the alcohol; while the high temperature mechanism (750-790°) consists of the polycondensation of the initial alcohol or some of its conversion products. During the polycondensation of acetaldehyde according to the low temperature mechanism, a series of elementary stages take place in succession: condensation, dehydration cyclization, the alternation of which in a definite order leads to the construction of polycyclic molecules of aromatic hydrocarbons and oxygen-containing derivatives, forming the basis of the resins and the carbon. It is of interest to extend the investigation to other alcohols, also.

In the present work we have carried out a comparison of the mechanisms of carbon formation during the decomposition of isopropanol, n-hexanol, and cyclohexanol on the same catalyst and within the same temperature range as we have already used for ethyl alcohol.

EXPERIMENTAL

The work was conducted according to the same method as formerly [1,2] using a flow-apparatus for the heterogeneous catalytic investigation, provided with a detachable quartz reactor, and operating at atmospheric pressure and a volume rate of introduction of the liquid reacting materials of 2.25 hr⁻¹. For each experiment a fresh portion of the catalyst was taken of volume 4 ml. The reactor with the catalyst was weighed on an analytical balance before and after the experiment. The carbon was determined by difference. Resinous products of polycondensation, which were deposited on the walls of the cold portion of the catalytic tube, were washed out with chloroform after the experiment, and also estimated quantitatively. Appreciable separation of resinous products on the walls of the vessel was observed only at experimental temperatures higher than 700°. Any resinous products which were contained in the low temperature carbonaceous material, and which were capable of being distilled away from this at increased temperature, were not determined by us separately. Under the heading of carbonaceous substance were included all the condensation products remaining on the catalyst at the conclusion of the experiment, after washing out for several hours with nitrogen at the experimental temperature. The alcohols used in the work were specially dried and redistilled. They had the following constants: isopropanol - b.p. 82° (758 mm); n_D^{20} 1.3774; d_4^{20} 0.7856; n-hexanol - b.p. 157.1° (751 mm); n_D^{22} 1.4172; d_4^{20} 0.8180; cyclohexanol - m.p. 22-24°; n_D^{22} 1.4662; d_4^{25} 0.9453. Aldehydes and ketones were determined by absorption in a solution of hydroxylamine hydrochloride and titration with alkali. Olefins in the catalyzate were determined by measuring the bromine number. Gases were analysed in a VTI gas analysis apparatus and in a thermo-gaseous chromatography apparatus. A qualitative investigation of the resinous material was carried out by means of its ultra-violet spectra.

Discussion of Experimental Results

Figure 1 gives the change in the rate of formation of the carboniferous substance during the decomposition of isopropanol, n-hexanol, and cyclohexanol. The same figure, for comparison, gives the corresponding curve for ethanol obtained earlier [1,2]. For ethanol the change in the rate of carboniferous material formation has been explained by us earlier by the existence of two mechanisms for this formation: the low- and high-temperature mechanisms. To explain the observed course of the velocity of carboniferous material formation in the cases now under considera-

tion, it is necessary, in addition, to postulate the existence of three mechanisms for the formation of these: the low temperature (from 200-600°), high temperature (above 750°), and the intermediate (from 600-750°). In distinction from ethanol, isopropanol, n-hexanol, and cyclohexanol show a third mechanism, intermediate between the low and high temperature processes. The temperature positions of the low and high temperature mechanisms are the same for all the alcohols investigated, including ethanol. It is evident that these two mechanisms exhibit general peculiarities.

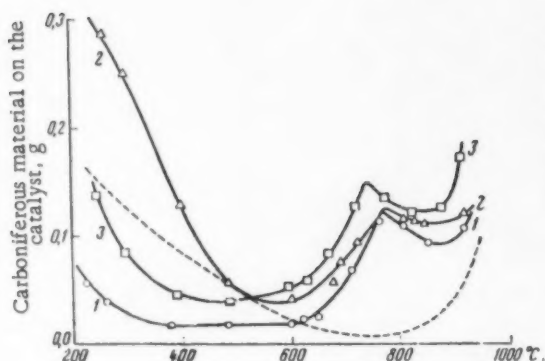


Fig. 1. Relationship between the carbon formation and the temperature in the decomposition of 1) isopropanol, 2) n-hexanol, and 3) cyclohexanol on a copper-silica-gel catalyst. The broken line gives the corresponding data for ethanol.

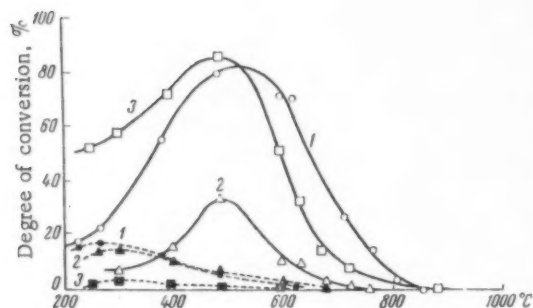
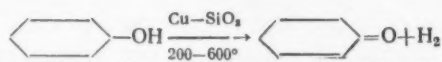
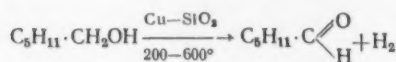
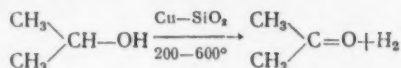


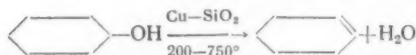
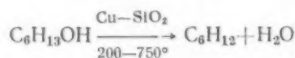
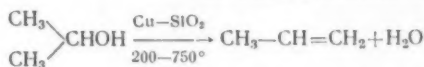
Fig. 2. Change in the rate of dehydrogenation (broken lines) and dehydration (solid lines) of 1) isopropanol, 2) n-hexanol, and 3) cyclohexanol on a copper-silica-gel catalyst with increase in temperature.

The low temperature mechanism of carbon formation for the decomposition of ethanol, as has been shown in [1,2], consists in the polycondensation of acetaldehyde previously produced through the catalytic dehydrogenation of the alcohol. For isopropanol, n-hexanol, and cyclohexanol the mechanism of the low temperature carbon formation, evidently, also consists in the polycondensation of acetone, hexylaldehyde, and cyclohexanone, previously produced through the catalytic dehydrogenation of the starting alcohols:



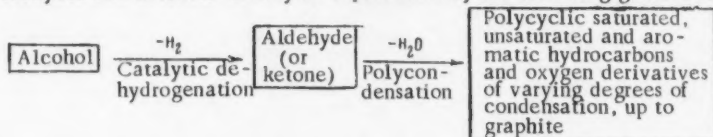
Evidence for this is found in the parallelism between the course in the rate of change of carbon formation according to the low temperature mechanism (cf. Fig. 1) and the change in the rate of dehydrogenation of the starting alcohols (Fig. 2). Here, where the rate of dehydrogenation is great, the rate of formation of condensation products is also great, and conversely. The low temperature mechanism disappears altogether under conditions in which, in addition to the dehydration of the alcohols, there takes place completely the competing process of dehydration (in the neighborhood of 600°), when aldehydes and ketones disappear in the reaction zone. For n-hexanol, which gives hexyl aldehyde, the rate of carbon formation is considerably greater than for cyclohexanol and isopropanol, which give ketones on dehydrogenation (cf. Fig. 1). This also confirms the reliability of the assumption concerning the mechanism of the low temperature carbon formation and of the polycondensation of the dehydrogenation products of the initial alcohols, since hexyl aldehyde would actually be more capable of polycondensation than the ketones.

In the temperature region of the low temperature mechanism, and above, the processes of catalytic dehydration of the starting alcohols take place with the formation of olefins:



It follows from Fig.1 and Fig.2. that, in spite of the development of dehydration processes when the temperature is increased to 500°, the rate of carbon formation diminishes and reaches a minimum exactly at the point of the maximum development of these processes.

These olefins are evidently not the starting material for carbon formation under the temperature conditions to which the low temperature mechanism applies; that is, the low temperature mechanism occurs simply through the polycondensation of aldehydes and ketones. It may be represented by the following general scheme:



This scheme is applicable to all the alcohols investigated by us, including ethanol. The polycondensation of aldehydes and ketones in the cases of isopropanol, n-hexanol, and cyclohexanol ought to consist (in a similar way to the polycondensation of acetaldehyde during the dehydrogenation of ethanol) of a multi-stage alternation of certain simpler reactions: condensation, dehydration, and cyclization. As a result of multiple repetitions of these reactions the formation and subsequent growth of increasingly complicated and increasingly high molecular weight products occurs.

When the temperature is raised above 600°, carbon formation may occur through the polycondensation of olefins, which arise as products of the dehydration of the initial alcohols. The rate of carbon formation according to this mechanism (which we have designated above as the "intermediate") increases with further rise in temperature.

TABLE 1. Composition of the Gaseous Products of the Decomposition of Alcohol on a Copper-Silica-Gel Catalyst.

Initial alcohol	Components of gas	Composition of gas, volume %, at temperature:							
		200°	300°	400°	500°	600°	700°	800°	900°
Isopropanol	H ₂	66	52	20	2	13	18	14	20
	CO	0	0	0	0	1.5	14	17	20
	C _n H _{2n+2}	0	0	0	1	2	30	48	50
	C _n H _{2n}	32	47	79	97	83	38	21	12
n-Hexanol	H ₂	100	91	75	48	9	12	15	26
	CO				1	6	14	18	15
	C _n H _{2n+2}				31	32	33	38	42
	C _n H _{2n}				7	50	42	29	17
Cyclohexanol	H ₂		100		89	30	16	18	30
	CO		0		0	2	18	17	15
	C _n H _{2n+2}		0		3	25	28	33	42
	C _n H _{2n+2}		0		9	42	42	30	10

The following facts demonstrate the probability of such an intermediate mechanism of carbon formation, which replaces the low temperature mechanism in the cases under consideration. The intermediate mechanism occurs up to 750°, within which range the products of the decomposition of the alcohols investigated contain appreciable quantities of propylene, hexylene, and cyclohexane (cf. Fig.2), and while the composition of the decomposition products remains practically uniform for all the alcohols (Tables 1 and 2). The existence of the intermediate mechanism is reflected also in the rates of formation of gaseous products (Fig.3). In the region where the intermediate mechanism occurs, a great rise in the rate of separation of gases is observed with increase in temperature, although in the low- and high-temperature mechanisms such rates are practically unchanged.

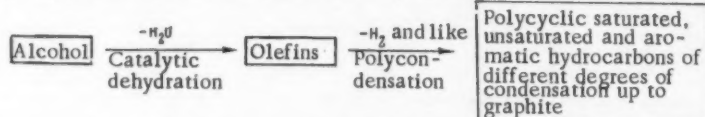
The postulate of the existence of an intermediate mechanism of carbon formation is further confirmed by the observation made by ourselves on the pyrolysis of n-hexane and n-heptane, cyclohexane and methylcyclohexane on silica-gel [3], in which it was noticed that one mechanism of carbon formation, consisting of the polycondensation of previously formed olefins, is replaced by another high temperature mechanism consisting of the dehydrocondensation of the initial hydrocarbons and the saturated products of their decomposition. It is interesting to note that the change

in the rate of carbon formation in changing mechanisms in the case of these hydrocarbons is closely reminiscent of the picture given by the change in the rates of carbon formation in moving from the intermediate mechanism to the high-temperature mechanism in the case of the alcohols studied.

TABLE 2. Composition of the Hydrocarbon Portion of the Gaseous Products of the Decomposition of Isopropanol and N-Hexanol on a Copper-Silica-Gel Catalyst (Thermogaseous Chromatography).

Initial alcohol	Temp., °C	Comp. of the hydrocarbon portion of gas, vol. %						
		CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₃ H ₆	C ₄ H ₈	C ₂ H ₂
Isopropanol	620	4	1	2	1	76		
	650	9	2	3	2	71		
	715	30	3	4	13	16		
	765	40	3	4	20	3		
	840	41	3	5	19	2		
	850	42	2	6	16	1		Traces
n-Hexanol	690	25	11	3	36	7		
	760	27	8	2	28	4	3	
	930	34	6	2	20	2		

The intermediate mechanism for carbon formation may be represented by the following general scheme:



This takes place, judging from Fig.1, under conditions in which dehydration of the alcohols occurs for isopropanol, n-hexanol and cyclohexanol, but is absent for ethyl alcohol; i.e., according to this mechanism, at temperatures from 600-750° polycondensation takes place with appreciable velocity for propylene, hexylene and cyclohexene, as well as probably the simpler higher olefins. Polycondensation of ethylene under these conditions may possibly also occur, but its rate is small, and only becomes appreciable at higher temperature, when the high-temperature mechanism is already in operation.

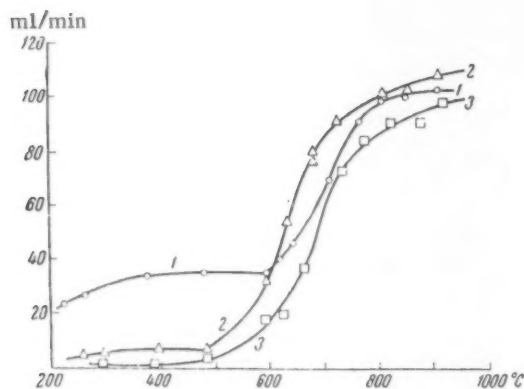
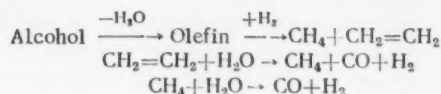


Fig.3. Rate of formation of gaseous products of the decomposition of 1) isopropanol, 2) n-hexanol, 3) cyclohexanol on a copper-silica-gel catalyst at various temperatures.

Shift from the intermediate mechanism of carbon formation to the high temperature mechanism is revealed in a sudden retardation of the process at temperatures above 750°. In the range 750-875° the rate of carbon formation slowly diminishes with increase in temperature, while above 875° it again increases rapidly. At the same time as the shift in mechanism occurs there is noticed an increase in the rate of formation of resinous condensation products (Fig.4), while two appreciable discontinuities in the rate are observed: one in the neighborhood of the beginning of the retardation of carbon formation (750°), and the other in the neighborhood of the new increase in the rate of carbon formation (875°). Simultaneously with the change in the mechanism, it is also observed, as has been remarked above, that the composition of the gaseous products of the decomposition of all the alcohols investigated becomes similar (cf. Tables 1 and 2) and the rate of formation of the gases is stabilized (cf. Fig. 3).

The decomposition of the alcohols at a high temperature, with the formation of gaseous products having approximately the same composition as each other, may be represented by the following scheme:



The gas composition in the cases considered is determined, strictly speaking, by the extent to which the conversion of ethylene and methane takes place in the presence of a definite quantity of water produced by the dehydration of the alcohol. The conversion of ethylene, judging by the data available on the gas composition, takes place more easily than that of methane, and the extent to which this takes place increases continuously with increase in temperature. The presence of small quantities of ethane and propane in the gases is apparently due to side processes in the cracking and hydrogenolysis processes for the olefins.

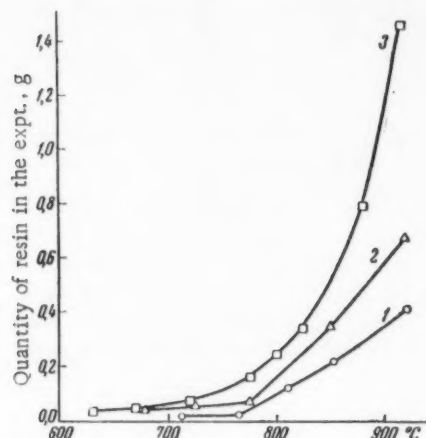
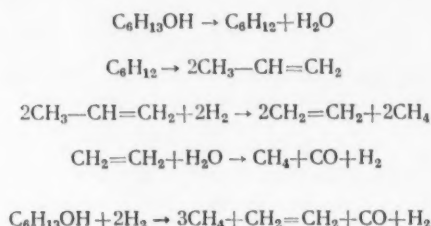


Fig.4. Change in the rate of formation of resinous substances during the decomposition of: 1) isopropanol; 2) n-hexanol; 3) cyclohexanol in the temperature range of the intermediate and high-temperature mechanisms for carbon formation.

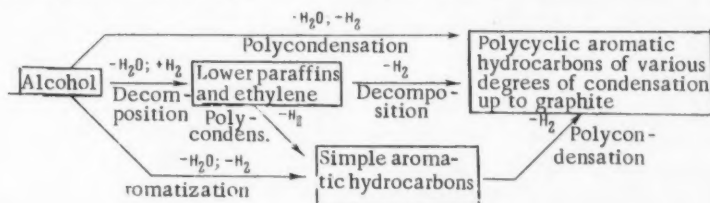
For example, for n-hexanol at 900° we have the gaseous composition: $3\text{CH}_4 + \text{CH}_2 = \text{CH}_2 + \text{CO} + 2\text{H}_2$, which, according to the scheme presented, corresponds to the following combination of reactions:



A corresponding suggestion may be presented also for the other alcohols, there being obtained a complete balance in all the components except the hydrogen, since the latter is formed not only as a result of conversion, but also in carbon formation.

From what has been set out above it is possible to represent the high-temperature mechanism as a dehydrocondensation of the simplest hydrocarbons from the composition of the gaseous products of the decomposition of the initial alcohols, principally saturated ones, and also of aromatic hydrocarbons previously obtained through the decomposition of the alcohols. However, as can be seen from a comparison of the rates of high-temperature carbon formation for the different alcohols (cf. Fig.1), the rates of these differ somewhat from each other by about 20-40%, which cannot be explained by the small difference in the composition of the products of the decomposition of these alcohols, whose compositions are practically identical. It must therefore now be assumed that in the high-temperature mechanism of carbon formation, side by side with the processes indicated above, the direct polycondensation of the initial alcohols into the carboniferous substance plays a significant part. This suggestion explains completely the observed differences in the rates of carbon formation, as due to the known peculiarities of the natures of each of the initial alcohols.

The high-temperature mechanism for carbon formation during the decomposition of alcohols at temperatures above 750°, can, apparently, be presented by the following general scheme:



This scheme has been applied to all the alcohols which we have studied, including ethanol. It represents a detailed consideration of the assumption concerning the mechanism of the high-temperature carbon formation discussed earlier by us [1] in the case of the decomposition of ethyl alcohol.

In distinction from the low-temperature and intermediate carbon formation mechanisms, the scheme presented as the final products of polycondensation, exclusively aromatic hydrocarbons. This is due to considerations of the practical impossibility of the formation of unsaturated, saturated, and hydroaromatic polycyclic systems under the conditions at which the high-temperature carbon formation mechanism operates, and is shown by the composition of resinous products of polycondensation in the case of all the alcohols studied, which have approximately the same composition and aromatic character, which is clear from what follows. The qualitative reactions of resins with sulfuric acid has shown, in all cases, the presence of polycyclic aromatic hydrocarbons. On the basis of the absorption spectra in ultra-violet light* it may be observed, by comparison of these with the published data [4], that the following substances are present in the resins: naphthalene, diphenyl, phenanthrene, anthracene, pyrene, perylene, triphenylene, benzpyrenes, dibenzperylene, chrysene, koronene, etc. No appreciable difference in the spectra was observed, and consequently the composition of the resins in moving from one alcohol to another is practically the same. From the resins obtained from each alcohol by means of fractional crystallization, naphthalene, diphenyl, and phenanthrene were obtained in pure form, having melting points of 80.4, 70.5, and 100.0°, respectively.

SUMMARY

1. In the decomposition of isopropanol, n-hexanol, and cyclohexanol on a copper-silica-gel catalyst, three mechanisms for carbon formation have been observed within the temperature range 200-950°.

2. A scheme has been presented for the mechanisms of carbon formation: a) the low-temperature mechanism (200-600°) is a polycondensation of the products of catalytic dehydrogenation of the alcohols (aldehydes and ketones); b) the intermediate mechanism (600-750°) is a polycondensation of the products of catalytic dehydration of the alcohol (propylene, hexalene, and cyclohexene); c) the high-temperature mechanism (750-950°) is a polycondensation of the products of decomposition of the initial alcohols (lower paraffins and ethylene), the polycondensation of aromatic hydrocarbons, previously formed in the decomposition of the alcohols, and the polycondensation of the initial alcohols themselves.

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* The spectra were obtained on a laboratory spectroscope from the Department of Organic Chemistry of Moscow State University on a spectrometer of type SF-4 in a cell of length 1 cm. Solutions of the resins in chloroform and in some other solvents were used, at a concentration of 0.000002 g/ml.

THE THEORY AND PRACTICE OF CONTINUOUS CHROMATOGRAPHY

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pp. 1938-1947, November, 1960

Original article submitted June 22, 1959

It is customary to assume that a discontinuity of the process is a specific characteristic of chromatography. However, in the separation of mixtures on a large scale it is desirable that the chromatographic equipment operate continuously. At first glance it seems simplest to pattern the construction of such equipment along the lines of extraction columns, i.e., with a counter flow of the powdered ionite and the solution. But movement of the solid phase unavoidably causes a longitudinal mixing of the liquid. This leads to a loss of the main advantage of the chromatographic method - the ability to obtain a large number of separation steps in a single and comparatively small apparatus. This disadvantage can be avoided if the counterflow of the solid sorbent is replaced by a counterflow of vessels filled with sorbent. The practicality of such a solution to the problem was shown in the work of Spedding, Powell, and Svec on the separation of the nitrogen isotopes [1].

The apparatus with a counterflow of the vessels (Fig.1) consists of consecutively connected sections - columns containing the ionite in the form of ion-predecessor. The zone of the mixture being separated is found in one of the columns. Under the influence of a stream of displacer ions the zone is transported from the first section into the second, then into the third, etc. If the selection of ion-predecessor and ion-displacer is done judiciously, then on move-

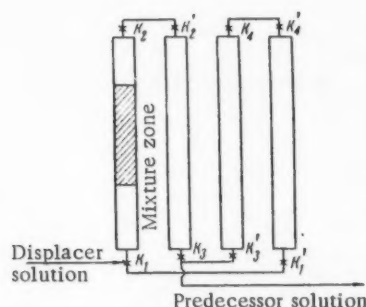


Fig.1. Diagram of chromatographic apparatus.

ment of the zone the mixture remains stationary and does not change either its size or shape. When the zone has moved into section 2, section 1 is disconnected and regenerated, i.e., it is converted from the ion-displacer form to the ion-predecessor form; the ion-displacer solution is admitted through stopcock K_2^* , while the ion-predecessor solution is discharged through stopcock K_4 . Section 2 is regenerated when the zone has moved into section 3; finally, the zone, emerging from section 4, is again fed into section 1, etc. In such an apparatus the zone of the mixture being separated can traverse a path of any length without deformation or diffusion, and here the components of the mixture are concentrated at different ends of the zone. A periodic removal of the separation products is begun when an equilibrium distribution of the components has been established. The point at which the zone passes from one section into the next is utilized to accomplish this periodic removal. Just as soon as the front end of the zone reaches the outlet, a certain amount of the substance, rich in the first component, is removed from the column. The starting mixture is introduced when the point of the zone with the initial concentration has passed through the connection and, finally, the mixture

rich in the second component is removed from the back end of the zone. A similar operation is repeated at each pass of the zone through the selected connection.

The problem as to the distribution of the components of a mixture along a stationary zone was solved by Bresler [2]. It was shown that the differential equation for nonequilibrium chromatography lends itself to linearization if the exchange constant K is sufficiently close to unity, i.e., if it can be represented as $K = 1 + \delta$, where $\delta \ll 1$. The tenets of the theory may be used with sufficient accuracy in the separation of close elements, where δ is 3-5 times smaller than unity. The conditions for obtaining nondiffusing zone fronts were formulated by Samsonov [3]. For equivalent ions it is necessary that

$$K_{12} \cdot \frac{\delta_1}{\delta_2} < 1,$$

*It is possible to follow the movement of the zone by measuring, for example, the electrical conductivity of the solution.

where K_{12} is the constant for exchange of the ion-predecessor by the ion following behind the front 2; and δ and δ_2 are the degrees of dissociation of the compounds of both ions in solution.

A critical concentration of the displacer exists for an accentuation of the front of ions with different valence:

$$c_{cr} = m_0 K_{12} \frac{\frac{z_1 z_2}{z_1 - z_2} \frac{\delta_1}{\delta_2} \frac{z_1}{z_1 - z_2}}{\delta_2 \frac{z_1}{z_1 - z_2}} \quad (2)$$

where z_1 and z_2 are the valences of the ions, and m_0 is the capacity of the sorbent. If the displacing is done by the ion with the higher valence, then to obtain a sharp and nondiffusing boundary it is necessary that the concentration of the displacer be $c_0 < c_{cr}$. On the other hand, c_0 should be greater than c_{cr} when the multivalent ion is displaced by the low-valence ion.

The operation of a chromatographic apparatus with withdrawal for the case where $\delta \leq 1$ is examined in the present paper.

Distribution of components of mixture along a stationary zone with a withdrawal regime. To be specific, we will solve the problem of the separation of a binary mixture in an apparatus with continuous withdrawal. Let q_k g-equiv/sec of mixture with a concentration of n_k of the first component be removed from one end of the zone. In order that the amounts of mixture and of first component in the zone remain constant, we will introduce a feed stream (q_0, n_0) at the point of initial concentration, while at the other end of the zone we will withdraw the waste product (q'_k, n'_k) (Fig.2). The conditions for retention of the amounts of mixture being separated and of the first component in the zone may be written in the following form:

$$q_0 = q_k + q'_k \quad (3)$$

$$q_0 n_0 = q_k n_k + q'_k n'_k$$

or

$$q_0 = \frac{q_k (n_k - n'_k)}{n_0 - n'_k} \quad (4)$$

$$q'_k = \frac{q_k (n_k - n_0)}{n_0 - n'_k}$$

If in each element of the zone the sorbent is found in thermodynamic equilibrium with the solution, then the following equation is valid:

$$\frac{m_1}{m_2} = K \frac{c_1}{c_2} \quad (5)$$

and the two conditions for a material balance are:

$$\begin{aligned} m_1 + m_2 &= m_0, \\ c_1 + c_2 &= c_0. \end{aligned} \quad (6)$$

where m is the number of gram-equivalents of the component sorbed by the ionite, referred to unit length of the column; c is the concentration of the component in solution, and c_0 is the concentration of the displacer solution; and m_0 is the exchange capacity of the ionite, referred to unit length of the column.

Combining (5) and (6), it is easy to obtain the following expression

$$\frac{n_s}{1 - n_s} = (1 + \varepsilon) \frac{n_l}{1 - n_l} \quad (7)$$

where n_l is the atomic concentration on the sorbent of the first component in the mixture, n_s is the concentration in the solution, and

$$\Delta n = n_s - n_l \cong \varepsilon n (1 - n). \quad (8)$$

In the system of coordinates relating to the zone there exists a counterflow of ionite and solution, in which connection the flow of mixture containing sorbent is equal to the solution flow

$$Q = vm_0 = \omega c_0, \quad (9)$$

where v is the transport rate of the zone along the column, and w is the space velocity of the solvent in the system of coordinates relating to the zone.

If the mixture on the sorbent and in solution has a different composition, then with a counterflow of the phases there arises an active transfer of the first component through the cross section of the zone

$$I_a = Q \Delta n. \quad (10)$$

The concentration of the first component begins to increase at one end of the zone and decrease at the other end - a concentration gradient arises along the zone also as the result of reverse diffusional flow

$$I_g \cong D^* \frac{\partial m_1}{\partial x}. \quad (11)$$

In total, the flow of the first component through a certain cross section of the zone is equal to

$$I = Q \varepsilon n (1 - n) - D^* \frac{\partial m_1}{\partial x}$$

or

$$I = Q \left[\varepsilon n (1 - n) - \frac{D^*}{v} \frac{\partial n}{\partial x} \right].$$

Actually, due to the absence in the chromatographic column of thermodynamic equilibrium between solution and ionite:

$$\delta n = n_s - n_L \leq \varepsilon n (1 - n),$$

$$I = Q \left[\delta n - \frac{D^*}{v} \frac{\partial n}{\partial x} \right].$$

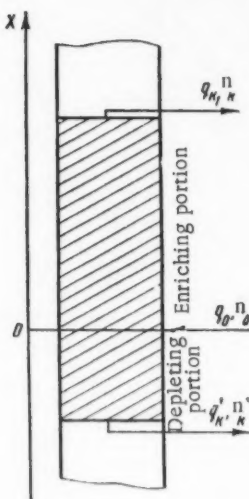


Fig.2.

Two approaches may be used to solve the problem of the distribution of the components of the mixture along the zone. An attempt may be made to determine the dependence of $\delta n + \Delta n$ on the characteristics of the chromatographic process, when D^* coincides with the convective diffusion coefficient D , but it is possible to assume that $\delta n = \Delta n$, and to regard the increase in the amount of nonequilibrium mixture by the streams of sorbent and liquid as some quasidiffusion process. As was shown by Bresler [2], in this case D^* - the quasidiffusion coefficient - is expressed very simply through the characteristics of the process:

$$D^* \cong \frac{\alpha c_0}{m_0} D + v^2 \tau \quad (12)$$

where α is the volume of the spaces between the sorbent granules, referred to unit length of the column, and τ is the time interval required to establish equilibrium between solution and ionite.

In the case of withdrawal, the expression for the flow of the first component through a certain cross section into the enriching portion of the zone should be written in the following form:

$$I = Q \left[\varepsilon n (1 - n) - \frac{D^*}{v} \frac{dn}{dx} \right] + q_h n \quad (13)$$

In the stationary state, such a concentration gradient will be established in the zone that the reverse diffusion flow will counterbalance all of the flow of the first component, with the exception of the withdrawn stream,

$$Q \left[\varepsilon n (1 - n) - \frac{D^*}{v} \frac{dn}{dx} \right] + q_h n = q_h n_k, \quad (14)$$

$$\frac{dn}{dx} = \frac{v}{D^*} \varepsilon n (1 - n) - \frac{v}{D^*} \cdot \frac{q_h (n_k - n)}{Q}.$$

Solving this differential equation, with the limiting condition $n|_{x=0} = n_0$

we obtain the following form:

$$\frac{k_1 - n}{n - k_2} = \frac{k_1 - n_0}{n_0 - k_2} \cdot e^{-\frac{(k_1 - k_2)}{D^*} \frac{\varepsilon v}{D^*} x}, \quad (15)$$

$$k_{1,2} = \frac{1 + \frac{q_k}{\varepsilon Q}}{2} \pm \sqrt{\frac{\left(1 + \frac{q_k}{\varepsilon Q}\right)^2}{4} - \frac{q_k n_k}{\varepsilon Q}}.$$

When $q_k \rightarrow 0$, the solution converts to the expression

$$\frac{1 - n}{n} = \frac{1 - n_0}{n_0} \cdot e^{-\frac{\varepsilon v}{D^*} x} \quad (16)$$

or

$$n = \frac{1}{2} \left[1 + \operatorname{th} \frac{\varepsilon (x - x_0)}{2 \text{HETP}} \right], \quad (17)$$

$$\text{HETP} = \frac{\alpha c_0}{m_0} \cdot \frac{D}{v} + v \tau,$$

where x_0 is the coordinate of the point with concentration $n = 0.5$, and HETP is the height equivalent to one theoretical plate.

The distribution of the components in the depleting portion of the zone may be found if in Equation (15) n_k and q_k are replaced by n'_k and q'_k , and n is replaced by $(1 - n)$. Equation (15) also makes it possible to calculate the length of the enriching portion of the zone l necessary to obtain q_k g-equiv/sec of mixture with concentration n_k :

$$l = \frac{D^* \ln \frac{(n_k - k_2)(k_1 - n_0)}{(k_1 - n_k)(n_0 - k_2)}}{\varepsilon v (k_1 - k_2)}. \quad (18)$$

It is easy to see that l has finite and actual values only when $n_0 > k_2$; or, assuming $n_k = 1 - a$, where $a \leq 1$, with the condition

$$Q > \frac{q_k}{\varepsilon n_0}.$$

Only in the case where $vm > gk / \varepsilon n_0$, in an apparatus with a zone of finite length, is it possible to produce q_k g-equiv/sec of product, enriched in the first component up to concentration n_k . The length of the mixed zone required to obtain q_k g-equiv/sec of rich product with concentration n_k , and of waste product with concentration n'_k is expressed by the formula:

$$L = F(Q) \cdot \frac{D^*}{\varepsilon v}, \quad (19)$$

$$F(Q) = \frac{\ln \frac{(n_k - k_2)(k_1 - n_0)}{(k_1 - n_k)(n_0 - k_2)}}{k_1 - k_2} + \frac{\ln \frac{[(1 - n'_k) - k'_2][k'_1 - (1 - n_0)]}{[k'_1 - (1 - n'_k)][(1 - n_0) - k'_2]}}{k'_1 - k'_2}.$$

Knowing the length of the zone, it is a simple matter to determine the total amount of sorbent R and the time required to establish a stationary distribution of the components in the zone:

$$R = L \cdot m_0.$$

If $\alpha c_0 / m_0 \leq v \tau$, which is valid at fairly moderate rates of zone transport, then

$$R = F(Q) \cdot Q \tau \quad (20)$$

It is very important that the amount of sorbent be determined only by the magnitude of the circulation flow of the mixture, and not by the transport rate of the zone.

To calculate the time required to establish a stationary distribution it is possible to make use of the formula obtained for a regime without withdrawal [2], since a withdrawal of the separated products is not made during the es-

establishing period:

$$T_y = \frac{L^2 \left(1 + \frac{\alpha c_0}{m_0}\right)}{\frac{\alpha c_0}{m_0} D + v^2 \tau} \left[\frac{1}{\pi^2 + \frac{(\epsilon v L)^2}{4 \left(\frac{\alpha c_0}{m_0} D + v^2 \tau\right)}} \right] \quad (21)$$

For a complete solution of the problem it is necessary to select the optimum flow of mixture, where the separation process will be the most economical. To simplify the problem we will examine the frequently encountered case, when $\epsilon \leq 1$, $n_0 \leq 1$, $n_k = 1 - a$, and where $a \leq 1$ and $l \geq l^*$. Then

$$k_1 \cong 1, \quad k_2 = \frac{q_k}{\epsilon Q}, \quad L \cong l \quad \text{and} \quad T_y \cong \frac{l^2}{\pi^2 D^*}.$$

It is easy to show that the losses of reagents for displacing* the zone and for regeneration, i.e., for conversion of the section from the form of ion-displacer to the form of ion-predecessor, are proportional to the flow Q . Actually, the space velocity of the solvent in the system of coordinates relating to the column is

$$\omega_0 = \omega + \alpha v$$

As a rule, in chromatographic apparatus $\alpha v \leq \omega$, and, consequently, $\omega \cong \omega_0$ and $Q \cong \omega_0 c_0$. On the other hand, the flow of regenerating agent should be equal to the flow of the displacer; otherwise, the cyclic operation of the apparatus is disturbed. When flow Q is decreased, the total losses of the chromatographic process are decreased, but at the same time the length of the zone L increases and, consequently, the time required to establish a stationary state (21).

The amount of displacer or of regenerating agent consumed in the process of operation of the apparatus is

$$P = Q (T_y + T_p), \quad (22)$$

where t_p is the time of operation of the apparatus in the stationary state. The consumption of reagents when the apparatus operates in the stationary state will be minimum at Q close to $K Q_{\min} = q_k / \epsilon n_0$. But here (18,21) the consumption of reagents during the establishing period, where the apparatus does not produce product, increases sharply

$$P_y = Q T_y = \frac{q_k \tau}{\pi^2 \epsilon^3} \cdot \frac{\ln^2 \frac{(1 - k_2)}{a(n_0 - k_2)}}{k_2 (1 - k_2)^2}. \quad (23)$$

P_y reaches its minimum value at k_{20} , being the root of the transcendental equation

$$\frac{1 - k_2}{a(n_0 - k_2)} = e^{\frac{2k_2}{(n_0 - k_2)(1 - 3k_2)}}.$$

The consumption of reagents when the apparatus is converted to the operating state will be minimum at

$$Q_0 = \frac{q_k}{\epsilon k_{20}}.$$

For example, for the case of the chromatographic separation of the nitrogen isotopes ($^{15}\text{NH}_4 + ^{14}\text{NH}_4 +$), when $n_0 = 0.004$, $n_k = 0.95$, $\epsilon = 0.0257$, $k_{20} = 0.0034$,

$$Q_{\min} = 250 \frac{q_k}{\epsilon}, \quad Q_0 = 300 \frac{q_k}{\epsilon}. \quad (24)$$

It is obvious that the magnitude of the optimum circulation stream should be confined to a fairly narrow interval

$$Q_{\min} < Q \leq Q_0.$$

A more exact selection of Q should be made on the basis of technological (length of the zone) and economic considerations (relationship between the establishing time and the time of operation of the apparatus).

In conclusion, we will examine the effect of periodicity of withdrawal on the distribution of the components of the mixture along the zone. As was mentioned above, in a real chromatographic apparatus the separation products are withdrawn only at the point where the zone passes through the connection between the sections. If the interval between withdrawals Q is much smaller than the time required to establish an equilibrium distribution of the compo-

* The losses for the creation of hydrodynamic flow during chromatography are always much smaller than the losses of chemical reagents.

nents of the mixture along the zone, then it is immaterial whether the withdrawal is made continuously (stream q_k) or in small portions, $N_k = q_k \theta$. Actually, as can be seen from Equation (21), at $\epsilon \leq 1$ the time of establishing a stationary distribution corresponds to the time of establishing diffusional equilibrium in a zone of length L at a diffusion rate proceeding with a coefficient of D^* ,

$$T_y = \frac{L^2}{\pi^2 D^*}.$$

We will assume that continuous withdrawal is replaced by intermittent removal at θ intervals. When withdrawal is terminated, the active transfer of the first component will be greater than the reverse diffusional flow (14) and the amount of the first component will begin to decrease at one end of the zone and increase at the other end. In time θ the disturbance of the concentration will spread from the ends by a length of the order of $\lambda = \sqrt{2D^* \theta}$. If $\theta \leq T$, then also $\lambda \leq L$.

Since the separation products, accumulating at the ends of the zone during interval θ , are removed at each consecutive withdrawal, then the intermittent nature of the process leads to periodic fluctuations of the mixture in the end elements of the zone - but the distribution of the components along the zone remains the same as in the case of operation with continuous withdrawal.

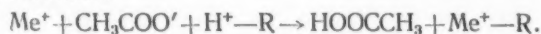
Continuous process of chromatographic separation of the alkali metals. To show that continuous chromatography is possible, we investigated the process of separating the alkali metals on the cationite SBS. The selection of this sorbent was not haphazard - the high rigidity* of SBS makes it suitable for column experiments with a cyclic change of the cations. On the other hand, in elutive chromatography the alkali metals are not separated on SBS resin [4].

Previously, in the course of studying the single act of the exchange of the alkali metal acetates with the sorbent, we determined the exchange constants and the time intervals τ . For the Na+Li mixture $K=1.53$, and for the K+Na mixture $K=1.55$. According to our measurements, for the Na+Li mixture, the time required to establish equilibrium between 0.5N acetate solution and SBS sorbent particles with a grain diameter of 0.1-0.3 mm was ≈ 80 sec.

To study the continuous chromatographic process we built a laboratory apparatus in which dead spaces between the sections were practically absent. The apparatus consisted of individual columns having a diameter of 2.5 cm. In each of the columns a layer of sorbent 10 cm high was placed on a porous glass filter. In the columns, densely packed with moist sorbent, the liquid was kept in the pores by capillary forces, but drops of the solution, falling from vessel A, percolated freely through the sorbent layer into the first column, descended into the second column, percolated further, etc. It is natural that in this manner the dead spaces between the sections were reduced to a minimum.

By measuring the electrical conductivity of the solution it becomes possible to follow the shape of both the front and the back boundaries of the zone and the distribution of the components of the mixture. For this purpose an S-shaped cell with electrodes was placed in one of the intervals between the columns. The change in the electrical conductivity was recorded automatically. By using mixtures of known composition to calibrate the apparatus it proved possible to determine the height, equivalent to one theoretical plate (HETP), and to investigate the dependence of HETP on the experimental conditions.

The economic outlays for conducting the continuous chromatographic process reduce mainly to outlays for regeneration of the spent sections, and to a large degree depend on the expeditious choice of displacer and predecessor. In the investigated case, the ion-predecessor was the hydrogen ion, while the displacer was the Ca^{++} ion in dilute acetate solution. The front end of the zone was sharpened due to the reaction for the formation of acetic acid, the degree of dissociation of which was considerably lower than that of the alkali metal acetates:



Thus, in the movement of the zone, the acetic acid was displaced continuously from the apparatus, while the ionite of the spent sections proved to be in the calcium form. In order that the zone of the mix-

*Rigid sorbents are those which do not change volume when the sorbed cation is changed.

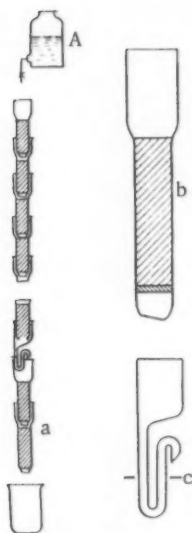


Fig.3. Apparatus for continuous chromatography: a) general appearance; b) individual section c) cell for measuring the electrical conductivity.

ture being separated always remains in the column, the upper sections in the Ca^{++} -form were removed periodically, while new sections, in the H^{+} -form, were substituted at the bottom. The regeneration process reduced to a washing of the ionite of the spent sections with 2N HNO_3 or HCl . The acetic acid flowing out of the bottom of the apparatus was simply neutralized with $\text{Ca}(\text{OH})_2$, after which the $\text{Ca}(\text{CH}_3\text{COO})_2$ solution was again recycled to displace the zone. Consequently, of the reagents, only HNO_3 and $\text{Ca}(\text{OH})_2$ were irrevocably consumed, while 2N $\text{Ca}(\text{NO}_3)_2$ solution was obtained as a waste product of the process.

The study was made using equimolar mixtures of $\text{Na}^{+}-\text{Li}^{+}$ and $\text{K}^{+}-\text{Na}^{+}$. The principal characteristics of the process for the displacement chromatography of these elements are given below: length of zone $L=40$ cm; total length of sorbent column = 150 cm; velocity of zone $v = 0.002-0.01$ cm/sec; salt concentration of displacer solution $c_0 = 0.5\text{N}$; volume capacity of sorbent = 1.5 mg-equiv/ml; and

$$\frac{ac_0}{m_0} = 0.25$$

By recording the curves for the change in the electrical conductivity over different intervals of the path, it becomes possible to study the process for establishing the distribution of the elements along the zone. It proved that a change in the concentrations of the components begins at the ends of the zones, then the disturbance spreads to the middle, and after a path of 1.5 m, a stationary boundary of separation between the ions of the mixture becomes established in the zone. The front end of the zone contains pure lithium acetate, and the back end contains sodium acetate. A similar picture was observed for the $\text{K}^{+}-\text{Na}^{+}$ mixture. The obtained zones of the alkali metals failed to change either their shape or their dimensions even after traversing a path of several tens of meters.

To determine HETP values, standard solutions of mixed alkali metal acetates, containing 25, 50, and 75% of the first component were placed in the cell for measuring the electrical conductivity. The marks obtained on the ribbon of the automatic recorder indicated the ordinates of the points with the corresponding composition on the electrical conductivity curve.

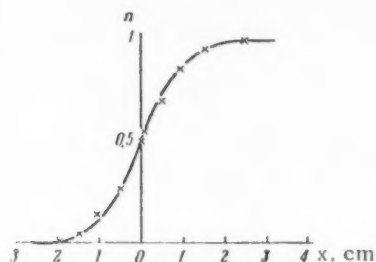


Fig.4. Typical boundary of separation between the alkali metals. The smooth curve was constructed using Equation (16); x = experimental points; $c_0 = 0.5\text{N}$; $v = 0.004$ cm/sec.

It is easy to determine the linear distance between the elements of the zone if the rate of zone movement is known:

$$= v \frac{d}{v_0}$$

where v is the velocity of the zone; d is the distance between the points on the ribbon of the automatic recorder, and v_0 is the travel rate of the ribbon of the automatic recorder.

If the distance between the points of the zone with a concentration of the first component ϵ of 25, 50, and 75% is known, then it is easy to calculate the HETP using Equation (16). Knowing HETP and ϵ , it becomes possible to construct the relationship

$$n = \frac{1}{2} \left[1 + \text{th} \frac{\epsilon (x - x_0)}{2\text{HETP}} \right]$$

The obtained curve coincides with the electrical conductivity curve, drawn on a corresponding scale. The experimental curve $\text{HETP} = f(v)$ is shown in

Fig.5. In its character it corresponds to Equation (17), which describes it.

The experiments on the displacement chromatography with withdrawal were run with both the velocity of the zone (0.003 cm/sec) and the concentration of the displacer ($c_0 = 0.5\text{N}$) kept constant. An S-shaped cell was used for both withdrawal and for feeding. The solution of the first component was withdrawn at the point when the front end of the zone passed through, the starting mixture was introduced at the point where the concentration was 50%, and the solution of the second component was withdrawn from the back end of the zone. To avoid contamination of the sample by calcium, the second withdrawal was not made from the extreme end of the zone, but instead, somewhat earlier. It is easy to select the point of withdrawal if the entire curve for the change in the electrical conductivity along the zone is taken in advance under analogous conditions.

Withdrawal was made at 4 hr intervals. The entire zone succeeded in passing through the cell in this length of time. The amount of material withdrawn was equal to 10 mg-equiv, and correspondingly 40 ml of 0.5N solution of

equimolar mixture was introduced into the middle portion of the zone. In the investigated case

$$q_k = \frac{10}{4 \cdot 3600} = 7 \cdot 10^{-4} \text{ mg-equiv/sec}$$

$$Q = \pi \frac{d^2}{4} \cdot m_0 v = \pi \cdot 1,96 \cdot 1,5 \cdot 0,003 = 2,7 \cdot 10^{-2} \text{ mg-equiv/sec}$$

$$k_1 \cong 1,$$

$$k_2 \cong \frac{q_k}{\varepsilon Q} = \frac{7 \cdot 10^{-4}}{0,53 \cdot 2,7 \cdot 10^{-2}} \cong 0,05.$$

In the separation of the $\text{Na}^+ - \text{Li}^+$ mixture the concentration of sodium in lithium, and the reverse, is equal to

$$\frac{n}{1-n} = e^{-\frac{L\varepsilon}{2\text{HETP}}}$$

$$n = 10^{-6}\%.$$

In the separation of the $\text{Na}^+ - \text{Li}^+$ and $\text{K}^+ - \text{Na}^+$ mixtures it is not unusual that spectral analysis fails to detect the presence of other alkali metals in the withdrawn solutions.

If the degree of purification is lowered to 99.9%, then, as before,

$$k_2 \cong \frac{q_k}{\varepsilon Q}$$

From Equation (15) it becomes possible to determine k_2 , assuming that the length of the enriching portion of the zone is equal to half of the total length. Then $k_2 \cong 0,5$, $q_k = 0,5Q$, and

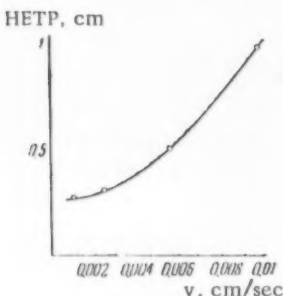
$$q_k \cong \frac{Q}{4},$$

As a result, 4 g-equiv each of nitric acid and of lime is consumed in the separation of 1 g-equiv of mixed alkali metals.

SUMMARY

1. A differential equation, describing the distribution of the components of a mixture along the zone in continuous displacement with withdrawal, was derived

Fig.5. Dependence of HETP on the travel rate at a displacer concentration of $c_0 = 0,5N$.



2. The continuous separation of the alkali metals $\text{K}^+ - \text{Na}^+$ and $\text{Na}^+ - \text{Li}^+$ was accomplished in a laboratory apparatus. The method of separation may be used to obtain very pure salts of the alkali metals.

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ADSORPTION AND HEAT OF ADSORPTION OF N-PENTANE AND OF N-HEXANE ON BARIUM SULFATE

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The adsorption properties of adsorbate-adsorbent systems are determined in a complex manner by many simultaneous factors, and among them are included the following factors associated with the structure of the adsorbent: nature of adsorbent, crystal structure or amorphous structure of its skeleton, porosity, chemical properties of the surface, and the degree of its geometric and chemical nonhomogeneity. This makes it difficult to study adsorbents and to generalize the obtained experimental data. For this reason a necessary part of studying the adsorption properties of complex adsorbents should be a study of adsorption on homogeneous surfaces; this facilitates elucidating the role of other complicating factors via a gradual transition to studying more complex cases. In our previous papers [1-5] we studied the adsorption and the heat of adsorption of a series of hydrocarbons on the homogeneous surface of graphitized soot, representing mainly the basic face of graphite, and also on the somewhat less homogeneous surface of coarse-pored magnesium oxide [4,6,7], representing mainly the (100) face, and also on magnesium hydroxide [6]. The present paper, being a part of this series of papers, is devoted to a study of the adsorption properties in the case where different faces of the crystal appear on the surface. We studied the adsorption and the heat of adsorption of two alkanes, n-pentane and n-hexane, on barium sulfate.

Barium sulfate is sharply different from graphite and from magnesium oxide in the structure of its crystal lattice. The surface of the crystals of this ionic adsorbent is formed by faces having different indices and with a dissimilar arrangement of the ions [8]. It is constructed from both large and small ions, and the complex SO_4^{2-} anions which enter into its composition, in comparison to the carbon atoms on the basic planes of graphite, and to the magnesium and oxygen ions on the (100) planes of magnesium oxide, are quite sparsely scattered on the surface.

EXPERIMENTAL

The barium sulfate was prepared the same as in [9,10]. Before experiment it was vacuum-dried at 250° for 15 hr. We determined its specific surface by the low-temperature adsorption of nitrogen vapors, using the BET method. When the area of a nitrogen molecule in a dense monolayer was $\omega_m = 16.2 \text{ \AA}^2$, the value of the specific surface was 8.1 sq m/g. This value was used to determine the absolute adsorption values of the hydrocarbons and the extent of filling up of the surface. The adsorbates, n-pentane and n-hexane, were used, the same as in [3]. The heat of adsorption of the vapors, as earlier, was measured in an automatic calorimeter with a constant heat exchange [11]. Admittance of the vapors into the calorimeter and measurement of the adsorption values were done by the volumetric liquid method using a vacuum capillary microburet [11]. The measurements were made at 20°.

The isotherms for the adsorption of the vapors of n-pentane and n-hexane on barium sulfate are shown in Fig. 1 in different scales. Three series of measurements were made for each vapor, and the measurement results coincided. The adsorption isotherms are reversible and convex at the start, and their shape is characteristic for the adsorption of vapors on nonporous adsorbents. At the start (up to a relative pressure of $p/p_s = 0.01$) the adsorption isotherm of n-hexane, in accordance with the greater energy of adsorption, proceeds above the adsorption isotherm of n-pentane, while in the region of higher p/p_s , the adsorption isotherm of n-pentane is the higher, in harmony with the horizontal distribution of the molecules of these hydrocarbons on the surface and the values of the areas ω_m , occupied by them in a dense monolayer.

The dependence of the differential heats of adsorption of the vapors of n-pentane and n-hexane on the amount adsorbed is shown in Fig. 2. From Fig. 2 it can be seen that in the embraced region of measurement of the extent of filling a sharp decrease in the heats of adsorption is not observed at the start*; the heat of adsorption remains practically

*When the extent of filling up the surface was less than 5%, the heat was not measured due to the experimental difficulties of calorimetric operation with such small surfaces.

constant, and then it decreases, slowly at the start and then with ever increasing rapidity; this decrease is slowed up only when the heat of condensation L is approached.

Thermodynamics of the Adsorption

Adsorption isotherm equations. Since the adsorption of these hydrocarbons on barium sulfate is accompanied by the evolution of much adsorption heat, the adsorbate-adsorbent interactions when compared with the adsorbate-adsorbate interactions are relatively great. In this case the more general equations of the isotherms of localized adsorption, taking into account the adsorbate-adsorbate interactions [12], are approximated by the simpler Langmuir and BET equations. Consequently, these equations were applied to the isotherms obtained for the adsorption of n-pentane and n-hexane on barium sulfate. The Langmuir equation describes both isotherms up to a filling up of the surface of $\theta = 0.5$, i.e., precisely that region of filling up where an approximate constancy of the differential heats of adsorption is observed (see Fig. 2). The BET equation describes both isotherms up to $\theta = 1.2$. The constants of these equations are given in Table 1.

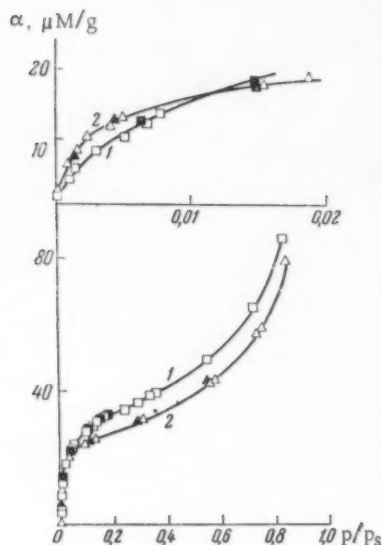


Fig. 1. Adsorption isotherms of vapors of n-pentane (1) and n-hexane (2) on barium sulfate. Here, and subsequently, the black points denote desorption.

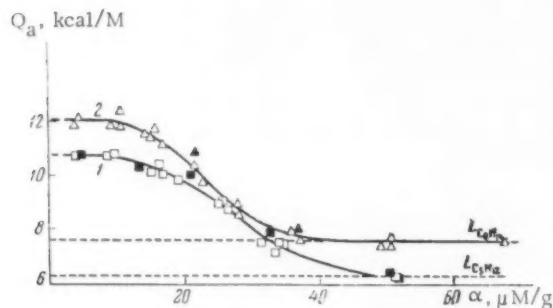


Fig. 2. Relationship between the differential heat of adsorption of vapors of n-pentane (1) and n-hexane (2) on barium sulfate and the amount adsorbed. The horizontal dotted line represents the latent heat of condensation L .

$$\omega_0 = \frac{191 \text{ \AA}^3}{4.0 \text{ \AA}} = 48 \text{ \AA}^2$$

and for n-hexane

$$\omega_0 = \frac{216 \text{ \AA}^3}{4.0 \text{ \AA}} = 54 \text{ \AA}^2^*.$$

*It should be mentioned that the structural peculiarities of the barium sulfate surface, the same as in the case of magnesium oxide [7], can also affect the packing of the nitrogen molecules, the adsorption of which was used to determine the specific surface at a value of $\omega_m = 16.2 \text{ \AA}^2$.

TABLE 1. Constants of the Langmuir and BET Equations, Characterizing the Adsorption Isotherms of n-Pentane and n-Hexane on Barium Sulfate

Adsorbate	Langmuir equation		BET equation		
	$a_m, \mu\text{M/g}$	K	$a_m, \mu\text{M/g}$	c	$\omega_m, \text{\AA}$
n-Pentane	25,6	140	27,8	190	~ 50
n-Hexane	21,6	380	22,7	300	~ 60

Both the Langmuir and the BET equations give close values of the capacity of the monolayer α_m , the adsorbate-adsorbent equilibrium constant K , and c . From the values of the capacities of the dense monolayer α_m , determined using the BET equation, we determined the area occupied by the n-pentane and the n-hexane molecules in the dense monolayer on the barium sulfate surface. It proved that these values are approximately 10-15% greater than the corresponding values (45 and 51.5 \AA^2) obtained for adsorption on graphitized soot. Apparently, this difference is explained by geometric factors exerting a different effect on the adsorption of nitrogen molecules and the molecules of these hydrocarbons. Cavities exist between the ions on the barium sulfate surface, and a part of the ion is raised. The tetrahedrons of the SO_4^{2-} ions are arranged differently with respect to the surface [8]. The comparatively larger serrated molecules of the n-alkanes fill up the barium sulfate surface less densely than in the case of graphitized soot, the surface of which represents a flat and close network composed of small carbon atoms. However, this peculiarity of the packing of the force centers exerts relatively little effect on the capacity of the monolayer. The areas ω_m , occupied by the molecules of n-pentane and n-hexane in the dense monolayer on barium sulfate, are close to the corresponding values calculated from the density of the liquid and the van der Waals thicknesses of the molecules (for n-pentane

Differential heat of adsorption. From Fig.2 it can be seen that the character of the curves for the dependence of the differential heats of adsorption on the amount adsorbed is the same for both vapors. The horizontal sections on the initial portion of the heat curves indicate the absence of a noticeable number of especially active heterogeneous sites on the surface. The increment for the heat of the adsorption in the initial region, when the hydrocarbon molecule is increased by one CH_2 group, is approximately 1.5 kcal/M *.

A comparison of the differential heats of adsorption of n-hexane vapor on barium sulfate with the corresponding values on graphitized soot and on magnesium oxide is presented in Fig. 3. When the degree of filling θ is approximately 0.2-0.5, the heats of adsorption on barium sulfate and on graphitized soot are close, while the heat of adsorption on magnesium oxide at these θ is considerably smaller. However, the general shape of the differential adsorption heat curves for graphitized soot resembles more closely the shape of the like curves for magnesium oxide. The dependence of the differential heats of adsorption on the degree of filling up of the barium sulfate surface is different.

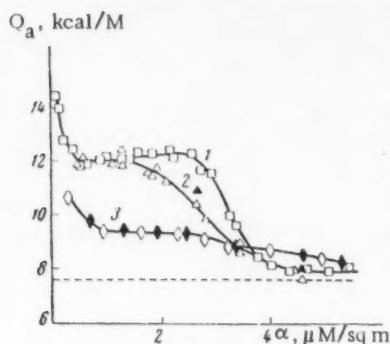


Fig.3. Differential heat of adsorption of n-hexane vapors as a function of the amount adsorbed on graphitized soot (1), barium sulfate (2), and magnesium oxide (3). The horizontal line represents the latent heat of n-hexane condensation L.

In the case of graphitized soot there is a small initial drop in the heat of adsorption due to some residual heterogeneity of the surface; subsequently, a rise in the curve is observed, associated with the additional evolution of heat due to side reactions of the molecules in the adsorption layer, and then a sharp decrease in the heat of adsorption occurs when transition is made from predominant adsorption in the first layer to predominant adsorption in the second layer. In the case of magnesium oxide, a closely similar course in the heat of adsorption is observed; only the initial heterogeneity of the surface is expressed somewhat more strongly, and, also, a rise in the heat of adsorption near the filling up of the monolayer fails to be observed, which is linked with smaller values of the adsorption heats (causing a less sharp transition from adsorption in the first layer to adsorption in the second layer), and, also, with a greater heterogeneity of the surface of this coarse-pored specimen.

Despite the closeness of the heats of adsorption at $\theta = 0.5$, the shape of the curve for the heat of adsorption on barium sulfate is quite different from that for graphitized soot in that the abrupt drop in the heat of adsorption does not begin near the completion of the monolayer, but instead considerably earlier - after one half of the surface has been filled. This is apparently explained by the above mentioned peculiarities of the crystallographic structure of the barium sulfate surface.

In the barium sulfate crystals, which belong to the rhombic syngony, the most developed are the (001), (110), (102), (011), and (104) planes [8]. All of these planes are characterized by a different and extremely complex arrangement of the Ba^{2+} and SO_4^{2-} ions on their surface and inside the lattice. At the start the adsorption of the hydrocarbons proceeds predominantly on the more developed faces with a large adsorption potential, and then the contribution of adsorption on other faces with a smaller adsorption energy becomes noticeable. This is the principal heterogeneity of the total surface of such crystals, composed of faces with different indices, and is probably the main reason for the decrease in the adsorption heat with filling up of the surface. In contrast to barium sulfate, graphitized soot contains mainly basic planes, while magnesium oxide contains mainly (100) planes, which assures a greater homogeneity of their surface.

The heterogeneity of the surface †, created by the very structure of the lattice and its nature, and not by a disruption of the surface structure of the face or by the presence of impurities, was clearly demonstrated in the studies of Young [14,15], who investigated adsorption on two crystalline modifications of potassium chloride. The shape of

*In [13] the dependence of the differential adsorption heat of propanol on the degree of filling up of the barium sulfate surface was calculated from isosteric coefficients, yielding the authors an initial adsorption heat for propanol equal to approximately 35 Kcal/M. Since, for the adsorption of methanol, this value is only ~ 18 kcal/M, then according to the data of [13] the increment for the CH_2 group is ~ 7 kcal/M, i.e., it exceeds the value found by us for the hydrocarbons in the calorimeter by a factor 5. The high propanol adsorption heat obtained in [13] also contradicts the determinations of the heats of wetting [10]. As a result, the value for the heat of adsorption of propanol on barium sulfate, equal to 35 kcal/M, is greatly exaggerated (by approximately 1.5 times).

† In our case the possibility of the effect of the heterogeneity created by the water, incompletely removed from the barium sulfate surface, remains unanswered.

the isosteric heats of adsorption as the surface of the cubic crystals of potassium chloride is filled up is characteristic for a homogeneous surface. For the rhombohedral modification of potassium chloride, which has two types of faces, each constructed from like ions, the effect of the crystallographic heterogeneity of the total surface and the stronger electrical fields of the faces leads to a sharp decrease in the heat of adsorption as the surface is filled up.

As regards the adsorbate-adsorbate interactions, then, the same as in the case of the adsorption of these hydrocarbons on graphitized soot and on magnesium oxide, with a filling up of the first layer this interaction is predominantly one of attraction. With a planar orientation of the molecules of these hydrocarbons, the heterogeneous and rapidly diminishing electrostatic field of the surface of the ionic lattice of barium sulfate is unable to create in them sufficient induced dipoles for a predominant manifestation of mutual repulsion [4,16].

Entropy of adsorption. On the basis of the obtained adsorption isotherms $\alpha(p/p_s)$ and the differential heats of adsorption $Q_a(\alpha)$, we determined the dependence of the differential changes in the free energy

$$\Delta\mu = \frac{d\Delta F}{d\alpha} = RT \ln p/p_s$$

and in the total energy

$$\frac{d\Delta U}{d\alpha} = -(Q_a - L)$$

on the adsorbed amount α , in which connection the pure liquid was taken as the standard state. From these values we calculated the dependence of the differential entropy of adsorption

$$\frac{d\Delta S}{d\alpha} = \frac{1}{T} \left(\frac{d\Delta U}{d\alpha} - \frac{d\Delta F}{d\alpha} \right)$$

on the degree of filling up of the barium sulfate surface. The curves for the differential entropy of adsorption of the vapors of n-pentane and of n-hexane pass into the negative region, forming minima near the point of filling up of the monolayer, and they have a similar appearance. The dependence of the differential entropy of n-hexane adsorption on the degree of filling up of the barium sulfate surface is shown in Fig.4. The corresponding curve for the adsorption of n-hexane on graphitized soot is also shown in Fig.4. Both curves have an analogous shape, but the barium sulfate curve is more diffuse, which is in agreement with the greater heterogeneity of the adsorption field of the surface of this specimen.

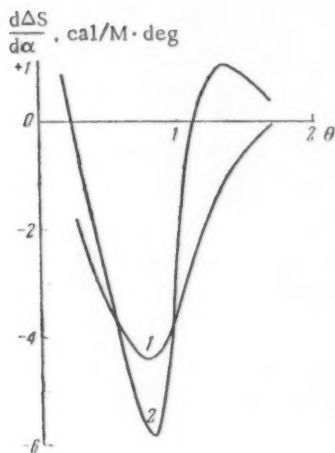


Fig.4. Dependence of the differential entropy of n-hexane adsorption on the degree of filling up of the surface of barium sulfate (1) and of graphitized soot (2).

Standard thermodynamic values for the adsorption of hydrocarbon vapors on barium sulfate. In Table 2 we have given the standard values (at $\theta = 0.5$) of the differential values of the heat Q_a° , total energy $(d\Delta U)/(d\alpha)^\circ$, free energy $\Delta\mu^\circ$, and the entropy of adsorption $(d\Delta S)/(d\alpha)^\circ$, and also the average molar change in the entropy of adsorption for filling up of the dense monolayer, ΔS_m .

TABLE 2. Standard Thermodynamic Characteristics of Adsorption of Vapors on Barium Sulfate at 20°

Adsorbate	Q_a° , kcal/M	$(\frac{d\Delta U}{d\alpha})^\circ$, kcal/M	$\Delta\mu^\circ$, kcal/M	$(\frac{d\Delta S}{d\alpha})^\circ$, kcal/M, deg	ΔS_m , kcal/M, deg
n-Pentane	10,6	-4,2	-3,0	-4,0	-4,0
n-Hexane	12,0	-4,4	-3,3	-3,7	-3,0

From Table 2 it can be seen that the entropy of adsorption is expressed by fairly large negative values, which suggests a decrease in the mobility of the adsorbate molecules when compared with their mobility in a normal liquid. Some decrease in the absolute change in the entropy, observed in going from n-pentane to n-hexane, may be due to an insufficient accuracy of the measurements, caused by the low value of the specific surface of barium sulfate.

Heat of wetting barium sulfate by n-alkanes. Integration of the curves of the differential net heats of adsorption of n-pentane and n-hexane gave the values of the net heats of saturation q_s equal to 68 and 60 ergs/sq cm, re-

spectively. As a result, the heat of wetting barium sulfate by these hydrocarbons is roughly 110-120 ergs/sq cm. It is considerably lower than the heat of wetting by water and alcohols [10].

SUMMARY

1. Using a calorimeter with a constant heat exchange, we measured the heats and the isotherms of the adsorption of n-pentane and n-hexane vapors on barium sulfate. The differential heat of adsorption of the hydrocarbon vapors shows little change up to where half of the surface is filled, and then it gradually decreases with increase in the degree of filling, due to the heterogeneity of the crystallographic faces forming the surface of the barium sulfate crystals.

2. The standard thermodynamic characteristics of the adsorption of n-pentane and n-hexane on barium sulfate were determined, as well as the values of the areas occupied by these molecules in a dense monolayer. The entropy curves testify to the substantial reduction in the mobility of the n-alkane molecules in the adsorption layer on barium sulfate when compared with their mobility in a normal liquid.

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ELECTRON-MICROSCOPIC INVESTIGATION
OF THE POROUS STRUCTURE OF ACTIVE CARBONS
USING THE REPLICA METHOD

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Active carbons were the subject of numerous investigations even in the comparatively early stages of the development of applied electron microscopy. In [1-4] it was mentioned that the electron microscope makes it possible to show the fine porosity of active carbons, and that a definite relationship is observed between the adsorption and the electron-microscopy data as regards the pore sizes of certain active carbon specimens. However, a serious limitation of these studies was the unsatisfactory preparation of the objects: the carbons were ground, for example, in a colloid mill [2] or in an agate mortar [4], dispersed in a liquid, and a drop of the obtained suspension was deposited on the film backing. Aggregation of the particles unavoidably took place when the liquid evaporated, and since, in addition, the degree of grinding the objects was not controlled, then the picture observed in the electron microscope could have little in common with the actual structure of active carbons. As a result, the imperfection of the method placed in doubt the scientific results of the investigations. It is obviously for this reason that such studies failed to receive further development.

Some forward progress in this respect was the dry preparation technique proposed by Luk'yanovich and Radushkevich [5]. By splitting the carbon grains the authors were able to obtain thin wedge-shaped plates, along the edges of which the retained structure could be observed. In the case of the sugar carbons, in harmony with the sorption characteristics, a highly developed transitional porosity was observed with pore sizes of the order of 100 Å. On the basis of studying the stereo electron micrographs, the authors expressed the theory that the transitional pores have a spherical shape and are connected with each other in the manner of the bulbs in a bulb condenser. Included among the basic disadvantages of splitting method, as well as of the method of ultrathin sections when applied to a study of active carbons, is the low degree of contrast of the image and, consequently, the low resolution obtained on the micrographs. In addition, the complex question arises as to what degree the effect of the mutual superimposition of the images of the pores found in different planes of the carbon sheet or cut is manifested.

Consequently, to study active carbons, the use of the replica method is the most promising, which in principle makes it possible to obtain a high-contrast image of the structure of the undisturbed surface layer of the sorbent, and which gives positive results in studying a number of other porous materials—silica gels, aluminosilicate catalysts, and titanium gels [6,7]. We used carbon replicas in the present study, the advantages of which over other variations of obtaining replicas have been discussed by Bradley [8]. The preparation technique in obtaining replicas from porous materials has been described in detail in the paper by Leont'ev and Luk'yanovich [9], and for this reason the method of study will be discussed in abridged form here.

EXPERIMENTAL

Since it is impossible to separate the carbon replica film directly from the active carbon, we were forced to resort to the two-stage method. The preparation was complicated by the brittleness and small size of the specimens (the carbons had a grain size of about 1 mm). For this reason, the most convenient technique proved to be prior pressing of the carbons into polyethylene. The grains were placed in a small (electrically heated) press mold between two blocks of polyethylene, after which the temperature was raised to 120° and a pressure of about 50 atm was applied. The specimen was then cooled without releasing the pressure. Under these conditions the polyethylene enveloped the specimen tightly, but it did not penetrate into the internal pores. The obtained block was then sliced with a razor blade in such manner that the plane of the cut passed through the carbon. Then a drop of 1% solution of collodion

in amyl acetate was deposited on the surface of the cut of the active carbon, followed in 2 hr by a drop of 5% solution. After evaporation of the solvent, a concentrated solution of collodion was also deposited in drops until a visible film with a thickness of 0.2-0.3 mm was formed, which was removed from the carbon using tweezers (removal of the film is facilitated by the poor adhesion of collodion to polyethylene). The deposition and separation of the film should be done 3-4 times until a clean imprint without adhering particles of carbon is obtained.

The so-called preshadowed carbon replica [7,8] was then prepared from the obtained intermediate collodion imprint. The relief side of the imprint was shadowed on both sides with platinum at an angle of 30° , and then the thinnest possible ($\sim 100\text{\AA}$) layer of carbon was deposited on top of the platinum by thermal evaporation. Prior to the most critical operation - removal of the replica from the imprint - the replica was first reinforced, molding a layer of gelatin 0.1-0.2 mm thick over the whole. Then the collodion was dissolved in acetone, after which the specimen was washed, dried, and the final replica was retrieved from the surface of warm water, in which the gelatin dissolved, and placed on the grid or object holder. The described method made it possible to obtain completely reproducible results for all of the investigated specimens.

For photographing we used an UEM-100 electron microscope with an electron magnification of 10,500. The resolving power of the microscope was 30 \AA .

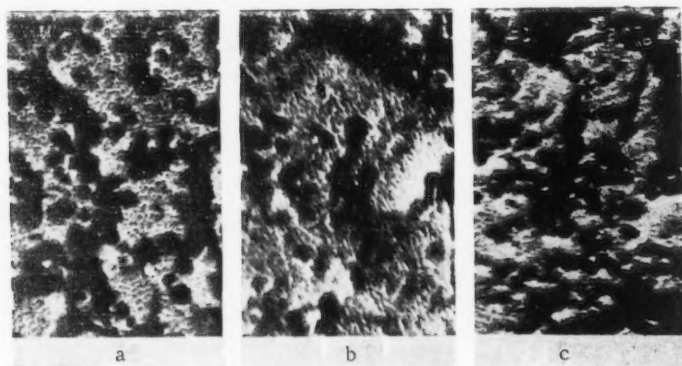


Fig.1. Carbon replicas from the surface of active carbons, obtained by the two-stage method. a) Specimen 1; b) specimen 2; c) specimen 3. $\times 60,000$.

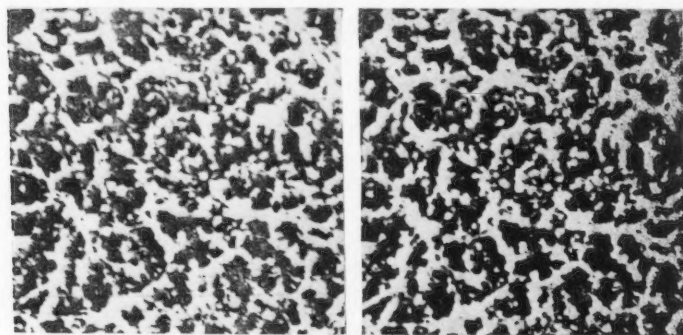


Fig.2. Carbon replica from an active carbon, Specimen 1. Stereo pair. Negative image, the interlinked light-colored round formations correspond to the macropores. $\times 20,000$.

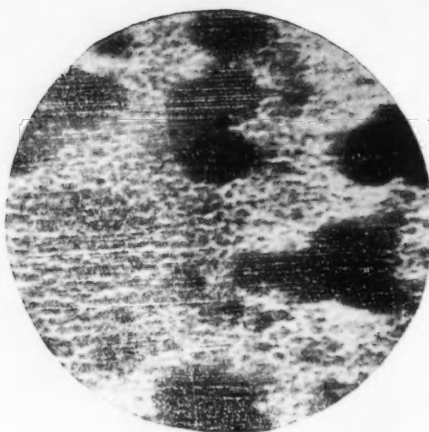


Fig. 3. Carbon replica from an active carbon, specimen 1. Transitional porosity at high magnification, $\times 150,000$.

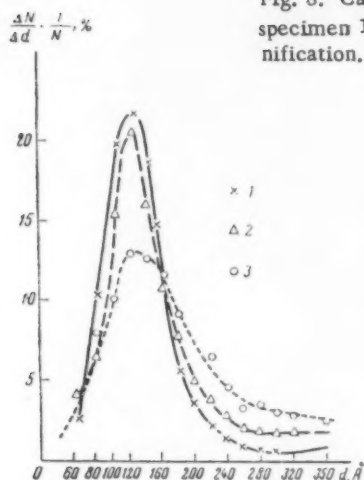


Fig. 4. Diameter distribution curves for the transitional pores of the active carbons: 1) Specimen 1; 2) Specimen 2; 3) Specimen 3.

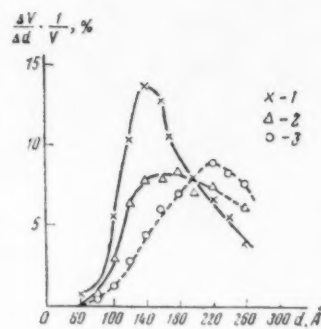


Fig. 5. Volume distribution curves for the transitional pores of the active carbons: X) Specimen 1; Δ) Specimen 2; O) Specimen 3.

Four specimens of active carbons served as the study objects. Of them, the first three, designated in the future as (specimens 1, 2 and 3, belonged to the same series, and were described by Dubinin and Zhukovskaya [10] as AU-10, AU-11, and AU-12, respectively. The specimens represented granular carbons with progressively greater activation, obtained from plant raw material and wood tar and activated to chars with an activity ranging from 35 to 60% using carbon dioxide at 950° . Specimen 4 was obtained by the zinc chloride method from sucrose and is described as AU-13 [10]. All of the carbons, according to the sorption data, possessed a highly developed transitional porosity which we hoped to show, using the electron microscope.

Actually, it was possible to clearly distinguish the porous structure of the carbons in all of the obtained micrographs. We will first discuss specimens 1-3. According to the visual observations, we obtained the same results for all of the specimens in this series (Fig. 1). The carbons possess a clearly defined bidisperse structure: together with comparatively coarse pores with a linear size of the order of 1000\AA , belonging to the class of macropores, it is easy to also see finer honeycombed pores, distributed in the walls between the macropores. The size of the finer pores is of the order of 100\AA and consequently they are typical transitional pores. That the system is bidisperse must be as-

sumed arbitrarily here, since the used electron-microscope method did not permit detecting the micropores present in the carbon with a size of the order of 10^{-7} cm, and also the possibly present very coarse macropores with a size of the order of 10^{-4} - 10^{-3} cm.

In order to give a more complete representation as to the structure of the macropores, we have shown in Fig. 2, under slight magnification, the negative image of the stereo pair of the carbon specimen 1. It should be emphasized that, in general, in interpreting the electron micrographs of systems with such a highly developed relief of the surface as exists in the case of active carbons, it is completely unnecessary to make extensive use of stereoscopy [7]. It is very clearly seen in Fig. 2 that the replica transfers the structure of the intermediate collodion imprint, filling the voids in the carbon, so that here the light-colored spherical particles, which are connected with each in a chain, projecting on the observer (the latter effect is achieved by the mutual shifting of the parts of the stereo pair to facilitate observation), correspond to the macropores. Consequently, the macropores in this series of carbons represent hollows that are spherical or nearly spherical in shape, connected with each other by narrower passages due to the absence of walls at the places of contact. Fig. 1 is also in complete accord with such a conclusion, where the projection of the structure on the plane is actually shown. The average diameter of the pores is ~ 800 Å. For this case it would be easy to obtain the pore distribution according to diameters and to compare it with the corresponding data using the method of forcing in mercury, but we did not deem this expedient in view of the presence of a large number of cracks of approximately the same size in the carbons. The question of why it proves possible to draw the intermediate collodion imprint, containing sections with periodically repeating constrictions and expansion, off the carbon remains somewhat obscure. Apparently, the carbon is partially chipped during this operation. In addition, it is possible for the elasticity of the collodion to play a part.

A more complex matter is a study of the transitional porosity of these carbons - due to the small dimensions of the pores, their images are less distinct and stereoscopy is not very effective here. Still, an examination at high magnifications of individual sections of the photographs (Fig. 3) makes it possible to compose a concept as to the structure of the transitional porosity. The latter resembles the structure of foam: thin walls separate the hollows, having in cross section the shape of a sphere or of a polygon*. Further, it can be observed that in some places the walls between adjacent pores are apparently either completely or partially absent. This makes it possible to understand the manner in which the pores may be connected with each other.

The dimensions of the transitional pores are so small that on the basis of the obtained microphotographs, it is impossible to obtain their reliable distribution according to size, all the more so since we used the two-stage replica method. Still in order to compare the carbons with different degrees of charring among themselves, we projected the images from the negatives at a magnification of 120,000, and by measuring the diameters of the pores we obtained the size distribution curves for the pores and then calculated from them (assuming a spherical shape for the pores) the volume distribution curves (Figs. 4 and 5). As can be seen from these plots, the greatest number of pores have a diameter of approximately 120 Å, and on increasing the degree of charring of the carbons some increase in the size of the pores is observed. The conditions of the electron-microscopic investigation were the same for all of the carbons, and, consequently, it could be assumed that the observed tendency possesses objective significance. A strongly developed transitional porosity can also be seen on the microphotographs of the sugar carbon replicas (Fig. 6). In contrast to specimens 1-3, well defined macropores do not appear here, while the transitional pores have somewhat larger dimensions. In other respects the structure of the transitional porosity is quite close to that of the earlier described carbons.

We made an attempt to use the method of ultrathin sections to study the porosity of the carbons. The specimens were covered with a mixture of butyl and methyl methacrylates (3:1), kept for 1 day to obtain deeper penetration of the liquid into the pores, and then the monomers were polymerized. From the polymerized blocks, using an ultramicrotome of the magnetostriction type with a glass blade [12], constructed in our laboratory, we prepared sections with a thickness of about 0.1μ . However, the microphotographs of the sections (Fig. 7) were decidedly inferior in both the degree of image contrast and the resolution of the replicas by the microphotographs. In addition, the sections proved to be highly inhomogeneous in thickness - individual sections were considerably thicker than the average thickness

* It is known [11] that a rectilinear polygon with n sides can be resolved on the microphotograph in the case where the condition of $\leq \pi d/4n$ is fulfilled, where δ is the resolution on the microphotograph, and d is the diameter of a circle, the area of which is equal to the area of the polygon. Since the resolving power of our microscope was 30 Å and the diameter of the pores was approximately 120 Å, then in the best case it could be expected to show the square cross-section of the pores.

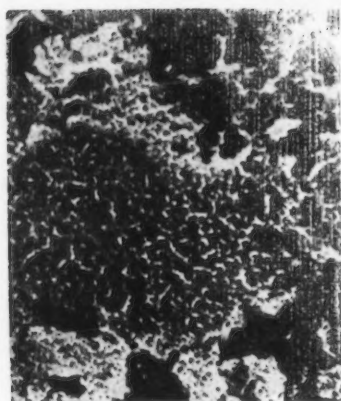


Fig. 6. Carbon replica from sugar carbon (specimen 4). $\times 60,000$.

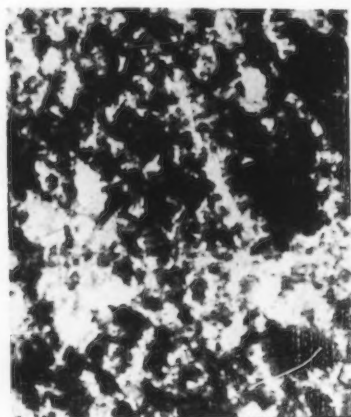


Fig. 7. Thin section of sugar carbon (specimen 4). $\times 35,000$.

of the cut, based on the rate of feeding the object during the cutting. Apparently, a partial tearing out of individual pieces from the specimen took place. The more brittle specimens (1-3) simply crumbled when cut, and for them it proved impossible to obtain satisfactory sections. We are of the opinion that the method of ultrathin sections can be useful in studying the macroporosity of active carbons if a more durable material is used to impregnate the carbons, fixing their structure, and also if a harder material, for example, diamond blades, are fused for cutting.

Discussion of Experimental Results

Very few ideas exist at the present time regarding the mechanism of the formation of the porous structure of active carbons. Depending on the conditions of preparation (composition of starting raw material, carbonization regime, and degree of activation), active carbons may possess a different character of the porosity. As had been shown in the studies of Dubinin and Co-workers [13], in the general case active carbons exhibit a tridisperse structure—three maxima exist on the total differential curve for the distribution of the pore volumes according to size, corresponding to the micro-, transitional, and macropores. This fact can be explained if the entirely probable assumption is adopted that the mechanism of the formation of each type of pore is different. Some of the earlier known data also testify in support of such an assumption.

A long time ago, Hofmann [14] assumed that the very fine pores in active carbons (i.e., micropores, according to the terminology of Dubinin) represent gaps or crevices between the elementary crystallites of the carbon. This makes it possible to understand why the dimensions of both are of the same order $\sim 10^{-7}$ cm. During activation a part of the crystallites burns out and the microporosity increases.

As regards the transitional pores, in [5] their spherical shape, established electron-microscopically, was explained by the conditions of formation: during the carbonization of the carbon-containing raw material, bubbles of gas evolve into the viscous medium, which, solidifying, is capable of fixing the foamlike structure formed. The more reliable electron-microscope data obtained in the present study by the replica method are fully in accord with the earlier obtained results. Thus, the slight change in the dimensions of the transitional pores for a series of carbons (specimens 1-3) again confirms the fact that the transitional porosity is formed during carbonization. Some development of the transitional pores during progressive activation is easily explained by a burning out of their walls. Apparently, the same mechanism should be applied to explain the spherical macropores in carbons 1-3. At the same time, these pores belong to a comparatively fine variety of macropores, since, usually, the maximum on the distribution curve for the

macropores lies in the region of the values of their effective radii of the order of 1μ [13]. Such macropores may represent cracks formed in the shrinkage of the carbon, or coarse canals for escape of the gaseous carbonization products, and, as was already mentioned, could remain undetected in the present study.

The manner in which the pores are connected with each other is a very important question. The electron microscopy data indicate that in the case of the macropores it is possible to assume with a greater, and in the case of the transitional pores with a lesser degree of probability, that the walls between the pores are absent at the places of contact. It is easy to represent the mechanism for the formation of such a structure. During carbonization a multitude of extremely fine gas bubbles are formed in a viscous liquid medium, which, increasing in size, come in contact with each other through the thin walls. The diameters of the bubbles at any given moment obey a definite distribution and in the general case two adjacent bubbles will differ in size, and, consequently, in the pressure of the gas inside of them. For this reason a rupture of the wall in the case of the bubble with the greater pressure should be expected. It is also possible that the partition between the bubbles, losing its elasticity because of the progressing carbonization process, in the final end will be torn by the increasing-in-size bubbles. If in this time the carbonization pro-

cess succeeds in progressing quite substantially, then the system acquires a rigidity and the arisen structure will be retained. To artificially produce carbons with a developed transitional porosity probably reduces to a creation of such conditions.

As a result, if in accord with the electron microscopy data the above presented concept is adopted, then the transitional pores should be connected by passages or necks with narrower diameters than the pores themselves, and the structure as a whole will resemble that of a bulb condenser *. A planar schematic drawing of such a structure is shown in Fig. 8; the micropores, naturally, will be found in the walls of the transitional pores. This structure is extremely close to a bottle-shaped form of the pores, assumed earlier as being possible for sorbents [16].

These concepts are found in harmony with the well known fact that the mercury forced into an active carbon in a pore meter is to a large degree retained in the sorbent after the pressure is removed [17], and that the pores, consequently, have a bottle-shaped form. On the other hand, it becomes clear that the pore diameters, determined using the electron microscope, and the effective diameters, calculated using the methods of mercury impregnation and of capillary condensation (based on the desorption branch of the isotherm), should relate to different portions of the described structure - the last two methods give values that relate to the necks of the pores, whereas the electron microscope permits measuring only the diameters of the spherical hollows. For this reason, with a sufficient accuracy of the methods it could be expected that systematically greater "electron-microscope" diameters would be observed for the different carbons when compared with the effective diameters, calculated using the last two methods. Establishing the presence or absence of such a rule would make it possible to judge more accurately the validity of the expressed ideas.

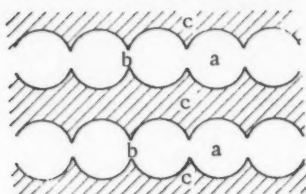


Fig. 8. Schematic drawing of structure of transitional porosity: a) transitional pores; b) necks; c) locations of micropores

Unfortunately, it is still impossible to quantitatively estimate the accuracy of the electron microscopy data. The difficulty of measuring small objects had already been indicated earlier: the magnitude of the error incurred in measuring, for example, particles having a size of approximately 100 Å with a microscope of the given resolving power has not been established up to now. Additional difficulties arise in connection with the fact that we used two-stage replicas. To be sure, carbon replicas are capable of reproducing the structure of the intermediate collodion imprint accurately, and to a depth of several microns, because of the lack of structure and the strength of the carbon film [8]. However, the question as to the accuracy with which the collodion imprint transfers the fine structure of the carbon remains to a large extent unanswered. In order to obtain an accurate answer to this question it is necessary to develop more perfect methods of preparation and to use a microscope with a higher resolving power.

SUMMARY

1. Using the two-stage replica method, we made an electron-microscopic study of the porous structure of some active carbon specimens. The method made it possible to establish the presence in the carbons of transitional pores and macropores in the form of spherical hollows.

2. The possible mechanism for the formation of transitional pores in active carbons and the character of their interlinkage are discussed.

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*Electron-microscopic investigations have shown that such a structure is characteristic for cellulose filters [15]. However, here the cross dimensions of the hollows are of the order of 1 μ.

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CRYSTAL AND MOLECULAR STRUCTURE OF PHENYLARSONIC ACID

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pp. 1962-1968, November, 1960
Original article submitted June 19, 1959

Deciphering of the structure. The crystals of phenylarsonic acid $C_6H_5AsO(OH)_2$ used by us for an x-ray study of the structure represent very fine yellow needles with a length up to 5 mm and a cross section of $\sim 0.1 \cdot 0.1$ mm. The needles are bounded by the four faces of a rhombic prism $\{201\}$ (b is the axis of the needles); the faces of the heads are not expressed. The parameters of the unit cell were determined by the oscillation method and the density was determined by hydrostatic weighing.

$$\begin{aligned} a &= 14.74 \pm 0.05 \text{ \AA} & M &= 202.03 \\ b &= 4.65 \pm 0.01 \text{ \AA} & d_{\text{meas.}} &= 1.86 \text{ g/cm}^3 \\ c &= 10.38 \pm 0.02 \text{ \AA} & d_{\text{x-ray}} &= 1.90 \text{ g/cm}^3 \\ V &= 711 \pm 3 \text{ \AA}^3 & n &= 3.92(4) \text{ } C_6H_5AsO(CH)_2 \end{aligned}$$

Systematic extinctions of the reflections of type $h00$ at $h \neq 0k0$, $0k0$ at $k \neq 2n$ and $00l$ at $l \neq 2n$, and the presence of piezoelectric properties, clearly define the space group $V^4 = P2_12_12_1$.

To determine the coordinates of the atoms, the $h0l$ and $hk0$ scans, respectively, containing 125 and 51 reflections of the measured intensity, were obtained when the reciprocal lattice was photographed (unfiltered Mo-radiation). The photographing was done using a backing of three films; in computing the intensities of the structure factors the Lorentz and polarization factors were taken into account, while the correction for absorption was neglected. The coordinates of the As atom were found from the ac and ab projections of the interatomic function. They were used to determine the first series of signs of the structure amplitudes. The subsequently computed projections of the electron density on the same faces of the cell disclosed all of the atoms of the molecule except hydrogen. The second series of signs was now found, taking into consideration all of the atoms, in which connection for C and O we used the atomic curves of Viervoll and Ogrim, and for As the curve from the "International Tables". These signs were used to compute the second approximation of the projections of the electron density. The coordinates from the second approximation led to the same signs, so that this approximation proves to be final. The structure amplitudes calculated from these coordinates were used to calculate the theoretical projections of the electron density, serving for introduction of the correction for Busse break in the coordinates of the second approximation; the final values of the coordinates, given in Table 1, were obtained in the same manner. In all cases the coordinates of the maxima were determined by exponential interpolation.

TABLE 1. Relative Coordinates of Atoms *

Atom	x	y	z	Atom	x	y	z
As	0.1262	0.1419	0.0848	C ₅	0.397	0.370	0.174
O ₁	0.109	-0.032	-0.063	C ₆	0.311	0.243	0.175
O ₂	0.057	0.409	0.121	H ₂	0.220	0.591	-0.079
O ₃	0.111	-0.120	0.203	H ₃	0.372	0.815	-0.081
C ₁	0.247	0.323	0.084	H ₄	0.486	0.673	0.081
C ₂	0.269	0.529	-0.009	H ₅	0.446	0.308	0.245
C ₃	0.355	0.656	-0.010	H ₆	0.294	0.084	0.247
C ₄	0.419	0.576	0.082				

*The coordinates of the hydrogen atoms were calculated using the conventional assumptions: C-H = 1.08 Å; C-C-H = 120°.

A comparison of F_{meas} and F_{calc} leads to the following authenticity factors and temperature corrections: projection ac - $R=9.6\%$, $B=3.47 \text{ \AA}^2$; projection ab - $R=13.6\%$, $B=3.65 \text{ \AA}^2$. Assuming that $R=b$ is the error of measuring the structure amplitudes, we find from the Weinsten equation the accuracy of determining the positions of the atoms: $As=0.002 \text{ \AA}$, $O=0.012 \text{ \AA}$ and $C=0.017 \text{ \AA}$. This leads to the following errors in the bond lengths: $As-O=0.012 \text{ \AA}$, $As-C=0.017 \text{ \AA}$, and $C-C=0.024 \text{ \AA}$. The valence angles are found with an accuracy of $\pm 2^\circ$.

The chemical identity of the investigated compound, originally erroneously assumed to be arsenobenzene (C_6H_5As), was established in the present study. A deciphering of the structure was begun assuming that the crystals are arsenobenzene, but the projections of the electron density each disclosed three "superfluous" maxima in the vicinity of the As atom. These same maxima also appeared persistently in the different projections (with the exception of the As atom), so that it was impossible to doubt their reality. For this reason it became obvious that the starting arsenobenzene had undergone important chemical changes during the process of purification and recrystallization, and specifically had oxidized to phenylarsonic acid.

The further deciphering of the structure was continued and was successfully consummated by considering the "superfluous" maxima to be O atoms. Thus, if they are not taken into consideration, then the authenticity factors increase sharply: R_{h0l} from 9.6 to 24.7%, and R_{hk0} from 13.6 to 24.9%. In addition, the large difference in the calculated and measured densities becomes admissible, while the distance $As-As \approx 5.0 \text{ \AA}$ does not correspond to a chemical bond.

The second approximation of the projections of the electron density on face ac is shown in Fig.1, where the maxima, corresponding to all the atoms of the phenylarsonic acid molecule, are seen distinctly.

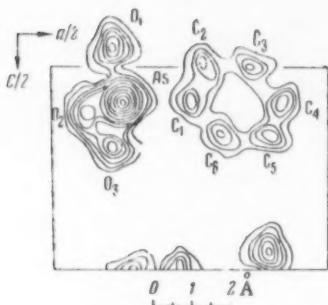


Fig.1. Second approximation of the ac projections of the electron density (relative units; the contour lines of the As atom are drawn half as often as in the other places).

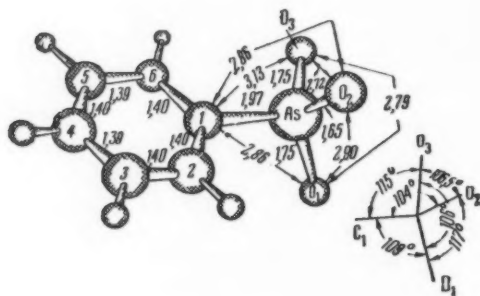


Fig.2. Phenylarsonic acid molecule.

Description of the structure. The bond lengths and the valence angles in the phenylarsonic acid molecule, computed using the coordinates in Table 1, are shown in Fig.2. The benzene ring is a flat rectilinear hexagon with sides equal to 1.40 \AA . The valence angles $As-C_1-C_2$ and $As-C_1-C_6$ are equal to 120° ; the bond length $As-C_1=1.97 \text{ \AA}$. In the literature [1] there are only two reliable measurements of the bond length $As-C$: $1.98 \pm 0.02 \text{ \AA}$ in $As(CH_3)_3$ and $(CH_3As)_4$, which is in good agreement with our result, representing the first determination of the bond length between As and aromatic hydrocarbon. The lengths of the $As-O$ bonds differ: $As-O_1=As-O_3=1.75 \text{ \AA}$, $As-O_2=1.65 \text{ \AA}$. For this reason it is possible to assume that atoms O_1 and O_3 are found as hydroxyl groups, while atom O_2 forms a double bond with As. This assumption is also supported by the distribution of the hydrogen bonds in the structure (see below). According to the literature data [2], the length of the $As-O$ bond varies from 1.75 to 1.80 \AA , in which connection in most of the investigated objects this bond has an intermediate character (single-double), but hydrogen bonds are absent in the structures. The values of the atomic radii taken from Pauling lead to the following lengths of the single and double bonds: $As-O=1.87 \text{ \AA}$, and $As=O=1.66 \text{ \AA}$.

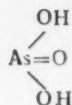
As a result, the length of the double bond $As=O$ does not change when oxygen atoms take part in hydrogen bonds, while the single bond is shortened by 0.12 \AA . An analogous effect was observed earlier in the structures of carboxylic acids having hydrogen bonds. Thus, for example, in the crystals of oxalic acid [3] and its dihydrate [4], $C=O=1.29 \text{ \AA}$ instead of the sum of the radii 1.43 \AA , while $C=O=1.19 \text{ \AA}$, with the sum of the radii equal to 1.25 \AA .

The valence configuration of arsenic is approximately tetrahedral, with substantial deviations of the angles $C-As-O$ and $O-As-O$ from 109.5° :

$C_1-As-O_1=109.0^\circ$	$O_1-As-O_2=117.0^\circ$
$C_1-As-O_2=104.0^\circ$	$O_1-As-O_3=106.0^\circ$
$C_1-As-O_3=115.0^\circ$	$O_2-As-O_3=106.5^\circ$

Average $109.5^\circ \pm 4.5^\circ$

These distortions of the valence angles cannot be related to a striving to decrease the steric hindrance in the group



and between it and the benzene ring. Actually, in the real molecule, the sum of the contractions $\Sigma\Delta$ of the distances between valently unbound atoms, when compared with the sums of the intermolecular radii ΣR , proves to be somewhat greater than in the molecule with ideal As valence angles, equal to 109.5° , and experimental values of the bond lengths. This can be seen from Fig. 2 and the following table, in which we have used the values of the intermolecular radii, computed from the distances in the given structure (see below):

$\Sigma R, \text{ \AA}$	$d_{\text{exptl.}}, \text{ \AA}$	$\Delta, \text{ \AA}$	$d_{\text{theor.}}, \text{ \AA}$	$\Delta, \text{ \AA}$
$\text{C}_1\text{---O}_1$ 3,09	3,03	0,06	3,04	0,05
$\text{C}_1\text{---O}_2$ 3,09	2,96	0,23	2,96	0,13
$\text{C}_1\text{---O}_3$ 3,09	3,13	—	3,04	0,05
$\text{O}_1\text{---O}_2$ 2,76	2,90	—	2,78	—
$\text{O}_1\text{---O}_3$ 2,76	2,79	—	2,86	—
$\text{O}_2\text{---O}_3$ 2,76	2,72	0,04	2,78	—
		$\Sigma\Delta=0,33 \text{ \AA}$	$\Sigma\Delta=0,23 \text{ \AA}$	

Consequently, the reason for the distortions of the As valence angles can only be intermolecular reaction involving hydrogen bonds, causing the As—O bonds to deviate from their ideal directions.

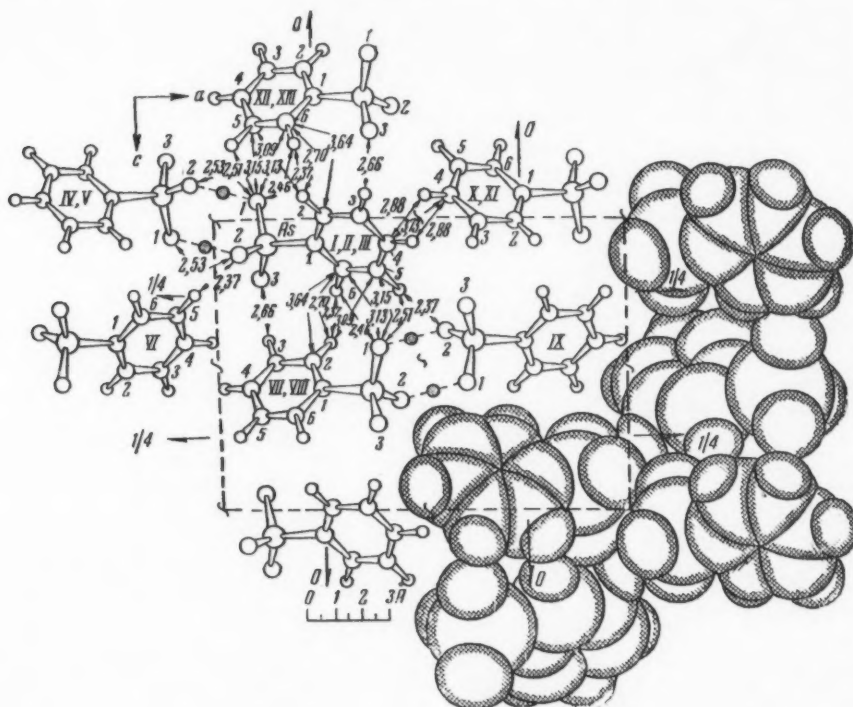


Fig. 3. Projection of the structure on face ac . On the right-hand of the diagram the molecules are framed by the intermolecular radii. Only one system of hydrogen bonds between the molecules, connected by the screw axis $2 \{OyO\}$, is shown.

The arrangement of the molecules in the crystal is illustrated by Figs. 3 and 4. The starting molecule (I) is in contact with 12 neighboring molecules (II-XIII), so that the coordination number is equal to 12. The adopted numeration of the molecules is as follows (the symmetrical bond between the given and starting molecules is indicated in parentheses).

- I: xyz (starting)
 II: $xy + 1z$ (translation b)
 III: $xy - 1z$ (a b)
 IV: $\bar{x}y + 1/2\bar{z}$ (axis 2_1 $[0y0]$)
 V: $\bar{x}y - 1/2\bar{z}$ (a 2_1 $[0y0]$)
 VI: $x - 1/2, 1/2 - y, 1/2 - z$ (axis 2_1 $[x\ 1/4\ 1/4]$)
 VII: $1/2 - x, \bar{y}, z + 1/2$ (axis 2_1 $[1/4\ 0\ z]$)
 VIII: $1/2 - x, 1 - y, z + 1/2$ (axis 2_1 $[1/4\ 0\ z]$ and translation b)
 IX: $x + 1/2, 1/2 - y, 1/2 - z$ (axis 2_1 $[x\ 1/4\ 1/4]$)
 X: $1 - x, y + 1/2, \bar{z}$ (axis 2_1 $[1/2\ y\ 0]$)
 XI: $1 - x, y - 1/2, \bar{z}$ (axis 2_1 $[1/2\ y\ 0]$)
 XII: $1/2 - x, \bar{y}, z - 1/2$ (axis 2_1 $[1/4\ 0\ z]$)
 XIII: $1/2 - x, 1 - y, z - 1/2$ (axis 2_1 $[1/4\ 0\ z]$ and translation b)

The contracted intermolecular distances, corresponding to the contacts of the molecules, are shown in Figs. 3 and 4 and in Table 2. All of the distances between the starting molecule I and its neighbors are indicated here. The contracted intermolecular distances lead to the following values of the intermolecular radii, used in all of the calculations given in the present paper: $R_c = 1.71 \pm 0.07 \text{ \AA}$; $R_o = 1.38 \pm 0.02 \text{ \AA}$; $R_h = 1.13 \pm 0.05 \text{ \AA}$. The natural volume of the molecules without taking into consideration the hydrogen atoms of the hydroxyl groups, forming hydrogen bonds, is $V_0 = 125 \text{ \AA}^3$; the packing coefficient $k = 0.70$.

Two of the O—O intermolecular distances undoubtedly correspond to stable hydrogen bonds; this is the O_1 (I)— O_2 (V) distance = 2.53 Å and the O_2 (I)— O_3 (II) distance = 2.48 Å. Both of these distances coincide with the lower limit for the average (for a large number of structures) distance of 2.5–2.7 Å between two oxygen atoms connected by a hydrogen bond [5]. Thus, atoms O_1 and O_3 each take part in one hydrogen bond, while atom O_2 takes part in two, which serves as additional argument in support of O_1 and O_3 belonging to hydroxyl groups. The arrangement of the hydrogen bonds is the following:

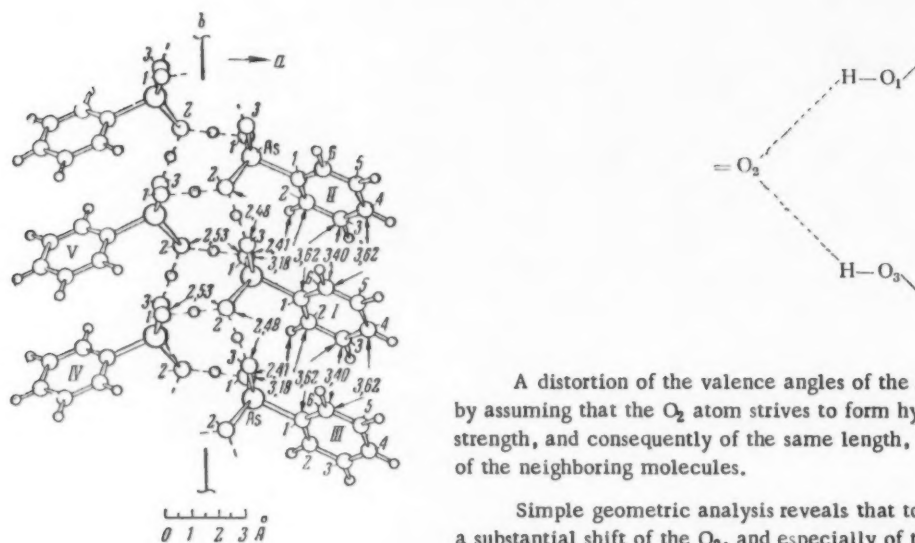


Fig. 4. Column of molecules, connected by hydrogen bonds (dotted line).

angles formed by the hydrogen bonds with the valence bonds of the oxygen atoms have the following values:



A distortion of the valence angles of the As atom can be explained by assuming that the O_2 atom strives to form hydrogen bonds of the same strength, and consequently of the same length, with the O_1 and O_3 atoms of the neighboring molecules.

Simple geometric analysis reveals that to accomplish this requires a substantial shift of the O_3 , and especially of the O_2 atoms from ideal positions, which is in agreement with the disclosed distortions of the valence angles. We encounter an analogous distortion of the valence angles due to striving to form stable hydrogen bonds, also, in the case of other structures, for example, oxalic acid [3] and its dihydrate [4]. The

It is entirely proper that for the O₂ atom, forming a double bond with As, these angles are close to 120°, while for the O₁ and O₃ atoms they are reduced.

The hydrogen bonds form two systems. The O₃-H...O₂ bonds connect the molecules, brought out from each other by translation b, into endless chains. Two such chains, connected by the screw axis $2_1 \{0y0\}$, are united by the hydrogen bonds O₁-H...O₂ into a compact column of molecules, stretched endlessly along axis b (Fig4). The entire structure may be regarded as a packing of such columns, based on the axes $2_1 [X 1/41/4]$ and $2_1 [1/4 0z]$. In each chain there exists a denser superposition of the benzene rings of neighboring molecules (distances C₆(I)-C₃=C₃(I)-C₆(III) = 3.40 Å. The perpendicular packing of the above mentioned columns also proves to be equally as dense.

TABLE 2. Intermolecular Distances (d) and Sums of Intermolecular Radii (ΣR)

Atoms	d, Å	Σ R, Å	Atoms	d, Å	Σ R, Å
C ₆ (I)---C ₃ (II)	3,40	3,42	C ₆ (I)---O ₁ (VII)	3,13	3,09
C ₆ (I)---C ₆ (III)	3,40	3,42	O ₁ (I)---C ₆ (XIII)	3,13	3,09
C ₁ (I)---C ₃ (II)	3,62	3,42	C ₅ (I)---O ₁ (VII)	3,15	3,09
C ₉ (I)---C ₁ (III)	3,62	3,42	O ₁ (I)---C ₆ (XIII)	3,15	3,09
C ₄ (I)---C ₆ (III)	3,62	3,42	C ₆ (I)---H ₂ (VIII)	2,70	2,84
C ₆ (I)---C ₄ (II)	3,62	3,42	H ₂ (I)---C ₆ (XII)	2,70	2,84
O ₁ (I)---C ₂ (II)	3,18	3,09	C ₆ (I)---H ₂ (VIII)	3,09	2,84
C ₂ (I)---O ₁ (III)	3,18	3,09	H ₂ (I)---C ₆ (XII)	3,09	2,84
O ₃ (I)---O ₃ (II)	2,48	3,47*	H ₆ (I)---O ₁ (VII)	2,46	2,51
O ₃ (I)---O ₂ (III)	2,48	3,47*	O ₁ (I)---H ₆ (XIII)	2,46	2,51
O ₁ (I)---H ₂ (II)	2,41	2,51	H ₆ (I)---O ₁ (VII)	2,51	2,51
H ₂ (I)---O ₁ (III)	2,41	2,51	O ₁ (I)---H ₆ (XIII)	2,51	2,51
O ₁ (I)---O ₂ (V)	2,53	3,47*	H ₃ (I)---O ₃ (XII)	2,66	2,51
O ₃ (I)---O ₁ (IV)	2,53	3,47*	O ₃ (I)---H ₃ (VIII)	2,66	2,51
O ₂ (I)---H ₆ (VI)	2,37	2,51	H ₂ (I)---H ₆ (XII)	2,37	2,26
H ₆ (I)---O ₂ (IX)	2,37	2,51	H ₆ (I)---H ₂ (VIII)	2,37	2,26
C ₂ (I)---C ₆ (XII)	3,64	3,42	C ₄ (I)---H ₄ (XI)	2,88	2,84
C ₆ (I)---C ₂ (VIII)	3,64	3,42	H ₄ (I)---C ₄ (X)	2,88	2,84
			C ₄ (I)---C ₄ (X)	3,73	3,42
			C ₄ (I)---C ₄ (XI)	3,73	3,42

*Sum of O-H bond lengths and intermolecular radii of H and O.

In conclusion the author feels it obligatory to thank M. Ya. Kraft for supplying the investigated compound, G. M. Lobanova for determining the piezoelectric properties of the crystals, and O. V. Starovskii for drawing the diagrams.

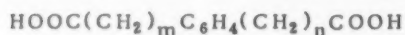
SUMMARY

1. The crystal structure of phenylarsonic acid was determined from two projections of the electron density.
2. The following bond lengths were found: As-C = 1.97 Å, As=O = 1.65 Å, As-O = 1.75 Å. The As atoms have a distorted tetrahedral valence configuration.
3. The molecular packing is determined by the stable hydrogen bonds -O-H...O = of length 2.48 and 2.53 Å, uniting the molecules into endless columns.

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THE SYNTHESIS OF DICARBOXYLIC ACIDS OF THE TYPE



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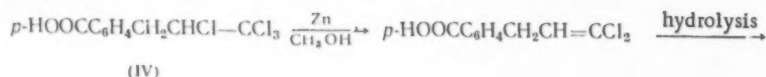
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As was shown in previous communications [1,2], 1,1,1-trichloro-1-propene and 1,1,3-trichloro-1-propene can be used for preparing various condensation products with aromatic compounds of the general type $\text{ArCH}_2\text{CH}=\text{CCl}_2$ and $\text{Ar}(\text{CH}_2\text{CH}=\text{CCl}_2)_2$. In the present work we describe the use of 1,1,3-trichloro-1-propene for the synthesis of dicarboxylic acids which contain an aromatic nucleus. Using nitromethane as the solvent we have carried out condensation in the presence of aluminum chloride of 1,1,3-trichloro-1-propene with phenylacetic, hydrocinnamic, and δ -phenylvaleric acids, and have obtained good yields of the corresponding products: $p\text{-HOOCCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ (I), $p\text{-HOOCCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ (II), $p\text{-HOOC}(\text{CH}_2)_4\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$.

The para-position of the substituents was shown by oxidation of these compounds to terephthalic acid which was identified as its dimethyl ester. Also, for the dimethyl ester of β,β' -(p -phenylene)dipropionic acid we took the infrared absorption spectrum which showed that in the region of the nonplanar oscillation of the CH group of the ring there is an absorption band characteristic only for para-substitution and not a characteristic frequency for ortho- and meta-substituents. By hydrolysis under mild conditions (long stirring with 88% sulfuric acid at room temperature) for compounds (I) and (II) we succeeded in converting them into 3-(p -phenylene)acetopropionic and β,β' -(p -phenylene)dipropionic acids, respectively. We did not succeed in hydrolyzing compound (III) since along with the hydrolysis there was sulfonation in the ring and desulfonation of the sulfo derivative by heating with dilute sulfuric acid or with hydrochloric acid.

The synthesis of β -(p -carboxyphenyl) propionic acid was carried out starting from 1,1,1,2-tetrachloro-3-(p -carboxyphenyl) propane [2] by the scheme:



The presence in the ring of substance (IV) of a carboxyl group also permitted carrying out its hydrolysis by sulfuric acid and obtaining a good yield of α -chloro- β -(p -carboxyphenyl) propionic acid, $p\text{-HOOCCH}_2\text{CH}_2\text{CHClCOOH}$.

As was shown by Nesmeyanov and Zakharkin [3], δ -chlorovaleric acid is easily condensed with benzene in the presence of aluminum chloride, leading to δ -phenylvaleric acid. Our attempt to carry out a further condensation of δ -chlorovaleric acid with δ -phenylvaleric acid ended unsuccessfully, since we could not find a satisfactory inert solvent in which we could dissolve the aluminum salt of the starting acid, and in which the reaction would occur with sufficient speed. p -Phenylenedivaleric acid was obtained with a yield of up to 30%, along with δ -phenylvaleric acid in the condensation of δ -chlorovaleric acid with benzene used in slight excess.

Previously [2] we obtained compound $p\text{-C}_6\text{H}_4(\text{CH}_2\text{CH}=\text{CCl}_2)_2$, which could not be converted to p -phenylene-dipropionic acid because of sulfonation in the ring during hydrolysis by sulfuric acid; we used it for preparing α,α' -dichloro- β,β' -(p -phenylene)dipropionic acid. The synthesis was carried out by direct addition of chlorine in anhydrous formic acid, according to the scheme:



EXPERIMENTAL

1,1,1,2-Tetrachloro-3-(p-carboxyphenyl)propane. ($\text{P}^-\text{HOOC}\text{C}_6\text{H}_4\text{CH}_2\text{CHCl}-\text{CCl}_3$). In a solution of 73.4 g (0.2 M) of $\text{p}-\text{CCl}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CHCl}-\text{CCl}_3$ [2] in 800 ml of acetone, with constant stirring, we repeatedly added small portions of KMnO_4 until the color did not disappear. The precipitate was filtered, washed three times with hot acetone, and dried; the resulting dry precipitate was extracted several times with boiling water. The combined water extracts were evaporated to 200 ml and acidified with hydrochloric acid. The acid which precipitated was recrystallized from alcohol, m.p. 194-195°; yield 43.5 g (72% of the theory).

The methyl ester was obtained by boiling the solution of this acid in methanol saturated with hydrogen chloride; colorless crystals, m.p. 83° (from heptane). Found: C 42.16; 42.23; H 3.02; 3.22; Cl 44.65; 44.61%. $\text{C}_{11}\text{H}_{10}\text{O}_2\text{Cl}_4$. Calculated: C 41.78; H 3.19; Cl 44.86%.

1,1-Dichloro-3-(p-carboxyphenyl)-1-propene ($\text{P}^-\text{HOOC}\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$). We dechlorinated 15.1 g (0.05 M) of $\text{p}-\text{HOOC}\text{C}_6\text{H}_4\text{CHCl}-\text{CCl}_3$ with zinc dust in methanol and obtained the acid, which after recrystallization from aqueous acetone, then from heptane, had m.p. 154-154.5°; yield 10.1 g (87% of the theory). Found: C 51.97; 51.68; H 3.47; 3.62%. $\text{C}_{10}\text{H}_8\text{O}_2\text{Cl}_2$. Calculated: C 51.97; H 3.49%.

The methyl ester had b.p. 125-126° (2 mm) n_D^{20} 1.5540; d_4^{20} 1.2960. Found: MR 60.61. $\text{C}_{11}\text{H}_{10}\text{O}_2\text{Cl}_2 \cdot 4 \text{ F}$. Calculated MR 60.32.

β -(p-carboxyphenyl) propionic acid ($\text{p}-\text{HOOC}\text{C}_6\text{H}_4\text{CH}_2\text{COOH}$). Hydrolysis of the acid $\text{HOOC}\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ (6.9 g) with 94% sulfuric acid was carried out at 70-80° for 15 min until evolution of hydrogen chloride stopped. The reaction mass was poured onto ice and the acid which separated was recrystallized from boiling water, m.p. 307-308°; yield quantitative. Found: C 61.53; 62.02; H 5.18; 5.19%. $\text{C}_{10}\text{H}_{10}\text{O}_4$. Calculated: C 61.85; H 5.19%. Literature [4]: m.p. 277-278°.

Dimethyl ester ($\text{CH}_3\text{OOC}\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{COOCH}_3$): m.p. 11-119° (from heptane). Found: C 64.17; 64.32; H 6.00; 6.13%. $\text{C}_{12}\text{H}_{14}\text{O}_4$. Calculated: C 64.80; H 6.35%.

α -Chloro- β -(p-carboxyphenyl)propionic acid ($\text{p}-\text{HOOC}\text{C}_6\text{H}_4\text{CH}_2\text{CHCl}-\text{COOH}$). Hydrolysis of 15.1 g of acid $\text{p}-\text{HOOC}\text{C}_6\text{H}_4\text{CH}_2\text{CHCl}-\text{CCl}_3$ with concentrated (96%) sulfuric acid was carried out at 120-130° for 45 min until evolution of hydrogen chloride stopped. The acid was separated as described in the previous experiment; yield 9.2 g (80% of the theory); m.p. 225-226° (from aqueous acetone). Found: C 52.30; 52.15; H 3.87; 3.86; Cl 15.77; 15.10%. $\text{C}_{10}\text{H}_9\text{O}_4\text{Cl}$. Calculated: C 52.53; H 3.97; Cl 15.51%.

Condensation of 1,1,3-trichloro-1-propene with phenylacetic acid (obtaining the acid $\text{p}-\text{HOOC}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$). To a solution of 54 g (0.4 M) of phenylacetic acid and 29 g (0.2 M) of 1,1,3-trichloro-1-propene in 50 g of nitromethane was gradually added with energetic stirring 60 g (0.45 M) of aluminum chloride. After addition of all the aluminum chloride the solution was heated on a water bath (80°) for 15 min, cooled, and poured on a mixture of ice and hydrochloric acid. The oil which precipitated was removed with benzene, the benzene extract was washed with hydrochloric acid and dried over calcium chloride. After distillation of the solvent and excess phenylacetic acid, the residue (40 g) was distilled in a vacuum. We obtained 33 g (67% of the theory) of acid ($\text{p}-\text{HOOC}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$); b.p. 147-148° (0.5 mm), m.p. 83-83.5° (from ligroin). Found: C 53.96; 54.13; H 3.98; 4.14%. $\text{C}_{11}\text{H}_{10}\text{O}_2\text{Cl}_2$. Calculated: C 53.99; H 4.11%.

The methyl ester ($\text{CH}_3\text{OOC}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$) was obtained by boiling a solution of the acid in methyl alcohol for two hours in the presence of several drops of concentrated H_2SO_4 ; b.p. 123-124° (1 mm); n_D^{20} 1.5400; d_4^{20} 1.2470. Found: C 55.29; 55.08; H 4.48; 4.44; Cl 27.19; 26.94%; MR 65.20. $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Cl}_2 \cdot 4 \text{ F}$. Calculated: C 55.61; H 4.67; Cl 27.36%; MR 64.94.

β -(p-Phenyleneacetic) propionic acid ($\text{HOOC}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{COOH}$). Hydrolysis of 12.3 g of $\text{HOOC}\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ was carried out by stirring the solution in 75 g of 88% sulfuric acid for many hours until evolution of hydrogen chloride stopped. The acid was separated in the usual way and recrystallized from hot water with addition of activated charcoal; fine, colorless needles with m.p. 183-184°; yield 4.7 g (45 of the theory). Found: C 63.39; 63.15; H 5.67; 5.58%. $\text{C}_{11}\text{H}_{12}\text{O}_4$. Calculated: C 63.45; H 5.81%.

Condensation of 1,1,3-trichloro-1-propene with hydrocinnamic acid (obtaining the acid $\text{p}-\text{HOOC}\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$). The reaction was carried out in nitromethane as in the case of phenylacetic acid. From 36.4 g (0.3 M) of 1,1,3-trichloro-1-propene and 90 g (0.6 M) of hydrocinnamic acid we obtained 56 g of condensation product. When this was vacuum distilled in a stream of nitrogen, we isolated the acid with b.p. 164-165° (1 mm) 154-156° (0.5 mm), n_D^{20} 1.5560; d_4^{20} 1.2757; yield 46.7 g (60% of the theory).

Found: C 55.60; 55.42; H 4.67; 4.66%; MR 65.29; $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Cl}_2 \cdot 4 \text{ F}$. Calculated: C 55.61; H 4.67%; MR 64.94.

The methyl ester ($\text{CH}_3\text{OOCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$): b.p. 125-126° (0.5 mm), n_D^{20} 1.5372; d_4^{20} 1.2209. Found: C 57.07; 57.36; H 5.18; 5.20%. MR 69.90. $\text{C}_{13}\text{H}_{14}\text{Cl}_2$. Calculated: C 57.16, H 5.17%; MR 69.55.

If the resulting condensation products were first esterified and then distilled in a vacuum, the yield was raised to 73% of the theory.

β, β' -(p-Phenylene)dipropionic acid [$\text{p-C}_6\text{H}_4(\text{CH}_2\text{COOH})_2$]. Hydrolysis was carried out with long stirring at room temperature of 13 g (0.05 M) of the acid $\text{HOOCCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ in a solution in 75 ml of 88% sulfuric acid until evolution of hydrogen chloride stopped. The product was recrystallized from methyl alcohol; m.p. 230°; yield 9.1 g (82% of the theory). Found: C 65.00, 64.93; H 6.37, 6.29%. $\text{C}_{12}\text{H}_{14}\text{O}_4$. Calculated: C 64.80; H 6.35%. The literature [5] gives m.p. 223-224° (from methanol).

The dimethyl ester was obtained by 5 minute heating of the acid in methyl alcohol with traces of sulfuric acid; m.p. 119-120° (from methanol); yield quantitative. Found: C 67.16, 67.01; H 7.17, 7.34%. $\text{C}_{14}\text{H}_{18}\text{O}_4$. Calculated: C 67.18; H 7.25%. The literature [5] gives m.p. 115° (from methanol).

Condensation of 1,1,3-trichloro-1-propene with δ -phenylvaleric acid (obtaining the acid $\text{HOOC}(\text{CH}_2)_4\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$). The reaction was carried out in nitromethane as in the case of phenylacetic acid. From 36.4 g (0.3 M) of 1,1,3-trichloro-1-propene and 107 g (0.6 M) of δ -phenylvaleric acid we obtained 69 g of condensation product from which vacuum distillation in a stream of nitrogen separated the acid with b.p. 180-181° (1 mm), n_D^{20} 1.5450; d_4^{20} 1.2166. Found: C 58.85; 58.71; H 5.66, 5.65; Cl 24.35, 24.51%; MR 74.63. $\text{C}_{14}\text{H}_{16}\text{O}_2\text{Cl}_2 \cdot 4 \text{ F}$. Calculated: C 58.55 H 5.62; Cl 24.69%; MR 74.18, yield 56 g (65% of the theory).

Boiling in methyl alcohol in the presence of a catalytic amount of sulfuric acid gave the methyl ester: b.p. 143-144° (1 mm), n_D^{20} 1.5290; d_4^{20} 1.1715. Found: C 60.19, 60.03; H 6.14, 6.24; Cl 23.34; 23.27%. Calculated: C 59.81; H 6.02; Cl 23.54%; yield quantitative.

δ, δ' -(p-Phenylene)divaleric acid [$\text{C}_6\text{H}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH})_2$]. In a solution of 102.5 g (0.75 M) δ -chloro-valeric acid in 150 g of benzene we gradually introduced 107 g (0.8 M) of aluminum chloride with stirring and outer cooling of the flask with ice water. After addition of all the aluminum chloride the mixture was heated to the beginning of energetic evolution of hydrogen chloride, then was heated for 15 min more in boiling benzene. The mixture soon thickened and another 100 g of benzene was added; the diluted mass was poured onto ice with hydrochloric acid. The benzene layer was washed with dilute hydrochloric acid and dried over calcium chloride. After distillation of the solvent and vacuum distillation of the residue, we obtained δ -phenylvaleric acid with b.p. 135-136° (2 mm); m.p. 59-60°; yield 70 g (52% of the theory) and 39 g of nondistilling residue. After triple recrystallization of the residue from methanol we obtained phenylenedivaleric acid with m.p. 180°; yield 32.3 g (31% of the theory). Found: C 68.79, 69.07; H 7.87, 7.90%. $\text{C}_{16}\text{H}_{22}\text{O}_4$. Calculated: C 69.04; H 7.97%. The literature [6] gives m.p. 179-182°.

The dimethyl ester was obtained by three hour boiling of the acid in methanol in the presence of several drops of sulfuric acid; b.p. 169-170° (about 0.5 mm), n_D^{20} 1.4975; d_4^{20} 1.0490. Found: C 70.15, 70.45; H 8.64, 8.45%; MR 85.54. $\text{C}_{18}\text{H}_{26}\text{O}_4 \cdot 3 \text{ F}$. Calculated: C 70.56; H 8.55%; MR 85.04. Literature data [7]: b.p. 182-184° (0.4 mm), m.p. 25° (from pentane).

Diethyl ester: b.p. 160-161° (0.1 mm), n_D^{20} 1.4920; d_4^{20} 1.0238. Found: C 72.12, 72.04; H 8.99, 9.05%; MR 94.77. $\text{C}_{20}\text{H}_{30}\text{O}_4 \cdot 3 \text{ F}$. Calculated: C 71.83; H 9.04%; MR 94.28.

α, α' -Dichloro- β, β' -(p-phenylene)dipropionic acid [$\text{C}_6\text{H}_4(\text{CH}_2 \cdot \text{CHCl}-\text{COOH})_2$]. A mixture of 29.6 g (0.1 M) $\text{C}_6\text{H}_4(\text{CH}_2\text{CH}=\text{CCl}_2)_2$ and 60 g of anhydrous formic acid was chlorinated at 35° with energetic stirring for two hours to evolution of 7 g of hydrogen chloride. The reaction mixture was diluted with water and the oil which separated was treated with a hot saturated soda solution. When the soda extract cooled, crystals separated and were filtered, dissolved in water, and the water solution was decolorized by boiling with activated charcoal. When the water solution of the salt was acidified an oil precipitated and soon crystallized. M. p. of the crude product 183-187°. After recrystallization from acetic acid, m.p. 199-200°; yield 8.7 g (30% of the theory). Found: C 49.28, 49.40; H 4.17, 4.11; Cl 24.10, 24.51%. $\text{C}_{12}\text{H}_{12}\text{O}_4\text{Cl}_2$. Calculated: C 49.50; H 4.16; Cl 24.36%. The literature gives [7] m.p. 165° (from hot water, first precipitating as an oil).

SUMMARY

1. Condensation of 1,1,3-trichloro-1-pentene with phenylacetic, hydrocinnamic and δ -phenylvaleric acids in the presence of AlCl_3 gave compounds with the structures $\text{p-HOOCCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ (I), $\text{p-HOOC}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ (II), and $\text{p-HOOC}(\text{CH}_2)_4\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CCl}_2$ (III).

2. Hydrolysis of compounds (I) and (II) by sulfuric acid gave acids with the structures $\text{HOOCCH}_2\text{C}_6\text{H}_4(\text{CH}_2)_2\text{COOH}$ and $\text{HOOC}(\text{CH}_2)_2\text{C}_6\text{H}_4(\text{CH}_2)_2\text{COOH}$.

3. Condensation of δ -chlorovaleric acid with benzene in the presence of AlCl_3 gave δ, δ' (p -phenylene)divaleric acid, along with δ -phenylvaleric acid.

4. By chlorination of the dichloroallyl derivative $p\text{-C}_6\text{H}_4(\text{CH}_2\text{CH}=\text{CCl}_2)_2$ in anhydrous formic acid we obtained an acid with the structure $p\text{-C}_6\text{H}_4(\text{CH}_2\text{CHClCO}_2\text{H})_2$.

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THE DECOMPOSITION OF ARYL DIAZONIUM BOROFUORIDES
IN NITROBENZENE AND ETHYL BENZOATE
IN THE PRESENCE OF THE FREE METAL, COPPER POWDER

L. G. Makarova and M. K. Matveeva

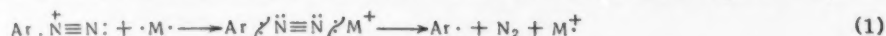
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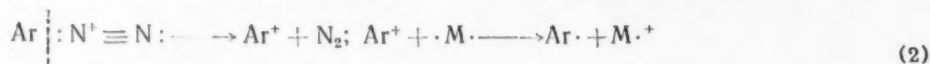
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In previous work [1] it was shown that aryl diazonium borofluorides in the absence of other diazonium salts, diaryl peroxides, and other sources of aryl radicals, decomposed in solvents with small dielectric constants heterolytically, with transfer of aryl cations in the reaction. We considered it unlikely that the synthesis of metalloorganic compounds (aromatic compounds of mercury, lead, tin, thallium, bismuth, germanium, magnesium) by the action of aryl diazonium borofluorides on free metals also took place by a heterolytic mechanism. It seemed probable that the synthesis of metalloorganic compounds through the aryl diazonium borofluorides took place by one of two possible paths: 1) under the influence of the metal the diazonium cation was converted to the diazo form and this split homolytically:



or 2) the metal reduced the product of heterolytic splitting of the diazonium salt, the aryl cation, converting it to the aryl radical:



In both cases the active agents in the formation of metalloorganic compounds are the aryl radicals.

In order to confirm the formation of aryl radicals in the synthesis of metalloorganic compounds from aryl diazonium borofluorides, we decomposed the aryl diazonium borofluorides in nitrobenzene, and phenyl diazonium borofluoride in ethyl benzoate in the presence of a free metal, copper powder. It was assumed that in the presence of free metal (copper powder) we would observe the products of homolytic action of aryl radicals on nitrobenzene and ethyl benzoate. In the first case there would be entrance of the aryl radical in all three positions of the nitrobenzene, chiefly in the ortho- and para-positions, but not excluding the meta-position, which occurs in decomposition of aryl diazonium borofluorides in nitrobenzene in the absence of copper. In the second case neither phenyl benzoate nor, as the sole product of entrance of phenyl in the ring of ethyl benzoate, an ester of meta-diphenylcarboxylic acid would be formed, as takes place in the decomposition of phenyldiazonium borofluoride in ethyl benzoate in the absence of copper, but there would be entrance of phenyl into all three positions of the ethyl benzoate, chiefly into the para- or ortho-positions. This would confirm our suggestion as to the mechanism of action of the metals on aryl diazonium borofluorides in the synthesis of metalloorganic compounds.

As expected, in the decomposition of aryl diazonium borofluorides (with the aryl being phenyl, para-tolyl, para-methoxyphenyl, para-chlorophenyl, ortho-carbomethoxyphenyl, and para-carboethoxyphenyl) in nitrobenzene in the presence of a large amount of copper powder, there were formed the products of the homolytic reaction; the aryls entered all three positions of the nitrobenzene, but chiefly the ortho- and para-positions. The reaction products were isolated by distillation and crystallization, and also were analyzed qualitatively by the method of ultraviolet spectroscopy. The decomposition of phenyl diazonium borofluoride in ethyl benzoate in the presence of excess copper powder was also completed by the homolytic mechanism, with formation of the products of the action of the phenyl radical on ethyl benzoate: in the reaction product we did not find phenyl benzoate even as a trace, and the chief product of entry of phenyl in the nucleus of ethyl benzoate was para-diphenylcarboxylic acid ethyl ester, with formation of the meta-isomer in slight amount.

In the decomposition in the presence of copper in nitrobenzene the aryl diazonium borofluorides, with the aryl being phenyl, para-tolyl, and ortho-carbomethoxyphenyl, we observed formation of products of entry of the aryl only in the para- and ortho-positions to the nitro group of nitrobenzene, namely: 4-nitrodiphenyl, isolated by distillation and crystallization; 2-nitrodiphenyl (shown by spectrophotometry in the ultraviolet), 4-methyl-4'-nitrodiphenyl and 4-methyl-2'-nitrodiphenyl; 2-carbomethoxy-4'-nitrodiphenyl, isolated by distillation and crystallization, and 2-carbomethoxy-2'-nitrodiphenyl (shown spectrophotometrically). Formation of the meta-isomer was not observed in these cases. The decomposition of 4-methoxyphenyl- and 4-chlorophenyl diazonium borofluoride gave products of entrance of the aryls into all three positions of the nitrobenzene, ortho-, meta-, and para-, and of these the ortho-isomer was formed in the greatest amount. We isolated by distillation and crystallization 4-methoxy-4'-nitrodiphenyl and 4-methoxy-3'-nitrodiphenyl. The presence of 4-methoxy-2'-nitrodiphenyl, 2'-nitro-, 4'-nitro-, and 3'-nitro-4-chlorodiphenyl was shown spectrophotometrically. In the decomposition of 4-carbomethoxyphenyl diazonium borofluoride we isolated as the chief product of entry into the nucleus 2-nitro-4'-carbomethoxydiphenyl, and the meta-isomer, 3-nitro-4'-carbomethoxydiphenyl was formed in less amount. In this case and in the decomposition of para-methoxy and para-chlorophenyl diazonium borofluoride we isolated from the reaction products the symmetrical azo compounds, the diethyl ester of azobenzene-4, 4'-dicarboxylic-acid, 4,4'-dihydroxyazobenzene, and 4,4'-dichloroazobenzene, respectively. Also, in two cases we isolated the ordinary products of thermal decomposition of aryl diazonium borofluorides: the diaryl (dimethyl ester of diphenic acid in the decomposition of ortho-carbomethoxyphenyl diazonium borofluoride) and a fluoroorganic compound (para-fluorobenzoic acid from the product of decomposition of para-carbomethoxyphenyl diazonium borofluoride).

Hence, the formation of the products of homolytic reaction in decomposition of aryl diazonium borofluorides in nitrobenzene, and ethyl benzoate in the presence of copper, confirms that the presence of the metal converts the heterolytic mechanism of splitting the aryl diazonium borofluorides into the homolytic. This forces us to assume the same action of metals on the mechanism of splitting of diazonium salts in the synthesis of metalloorganic compounds from aryl diazonium borofluorides, and perhaps also from other diazonium salts. The formation along with the diphenyl derivatives of symmetrical azo compounds also, suggests evidently, the use of the first of the possible paths of splitting the diazonium salts (equation 1).

EXPERIMENTAL

Decomposition of phenyl diazonium borofluoride in nitrobenzene in the presence of copper. In 160 g (1.36 M) of nitrobenzene at 28° we added over the course of half an hour in small portions, alternately, 90 g (1 M) of phenyl diazonium borofluoride and 50 g of copper powder prepared according to Gatterman. No marked rise in temperature occurred, but from the first portions the reaction mixture darkened. It was stirred for 72 hours, after which the reaction for diazonium compound was negative. It was dissolved in benzene, filtered from the copper (there were no lumps of tar), the benzene solution was washed with water, the benzene was distilled off, and the residue was fractionated in a vacuum. After distillation of the first quantity of nitrobenzene, we obtained: fraction I with b.p. 110-170° (3 mm), 4.8 g; fraction II with b.p. 170-200° (3 mm), 0.8 g. Fraction II gradually crystallized and after recrystallization from heptane the m.p. and mixed m.p. with known para-nitrodiphenyl was 113°. From fraction I, after repeated distillations we separated 2.3 g of nitrobenzene and at 2-3 mm and 125-270° we distilled 2.2 g of oil, which was submitted to qualitative spectrographic analysis in the ultraviolet in isooctane solution (SF-4 spectrophotometer of the Dianov-Klovov system). Optical analysis (qualitatively $\nu_{\max}=43,000\text{ cm}^{-1}$, $\epsilon \cdot 10^{-4}=0.5$) showed that this oil absorbed like the ortho-isomer ($\nu_{\max}=43,000\text{ cm}^{-1}$, $\epsilon \cdot 10^{-4}=1.6$), only less intensely. As a result of running a similar decomposition under analogous conditions (ratios of components, temperature, length of reaction) of phenyl diazonium borofluoride in nitrobenzene in the absence of copper, we obtained only meta-nitrodiphenyl.

Decomposition of para-tolyl diazonium borofluoride in nitrobenzene in the presence of copper. In 250 g (2 M) of nitrobenzene at 28° in the course of an hour with stirring we added, alternately, 104 g (0.5 M) of para-tolyl diazonium borofluoride and 50 g of copper powder. Almost no rise in temperature occurred. In the following five days the reaction mixture was heated to 50-55°, and the reaction then went on at room temperature. All the diazonium compound was decomposed (test with β -naphthol) after a month. The mixture was dissolved in benzene and filtered from tar and copper powder. The precipitate of tar and copper powder was made alkaline and submitted to distillation with superheated steam (bath temperature 220°). We distilled over 0.8 g of crystals. After crystallization from acetone the m.p. and mixed m.p. with known 4-methyl-4'-nitrodiphenyl was 140°. The filtrate from the precipitate of tar and the powder was washed with 10% NaOH, with water, and was dried with CaCl_2 . After distillation of the benzene and (in a vacuum) of most of the nitrobenzene, the residue was distilled with superheated steam (bath tempera-

ture 220-240°). The distillate was extracted with ether, the ether was distilled off, and the residue was fractionated in a vacuum. We obtained the fractions: fraction I with b.p. 75-110° (4 mm), 2.9 g; fraction II with b.p. 150-175° (4 mm), 3.76 g; fraction III, b.p. 175-182° (4 mm), 3.0 g.

Fraction I after repeated distillations (b.p. 45-46° at 3 mm) was shown to be nitrobenzene. Fraction III crystallized; after crystallization from methyl alcohol the weight was 2.3 g, the m.p. and mixed m.p. with known 4-methyl-4'-nitrodiphenyl was 140°. Fraction II did not crystallize when cooled with snow and salt. It was combined with the mother liquors from crystallization of the precipitate of Fraction III and the products of distillation of the tar. After distillation of the solvent it was distilled in a vacuum and gave 3.6 g of oil with b.p. 140-150° (2 mm). Part of the oil was diluted with heptane; on slow cooling there precipitated crystals with m.p. 34°; a mixed m.p. with known 4-methyl-2'-nitrodiphenyl was 34-36°. The oil (b.p. 140-150° at 2 mm) from qualitative spectroscopic analysis in the ultraviolet (solvent isooctane, $\nu_{\max} = 41,000 \text{ cm}^{-1}$) was also 4-methyl-2'-nitrodiphenyl ($\nu_{\max} = 41,000 \text{ cm}^{-1}$) and did not contain meta- and para-isomers.

Decomposition of para-methoxyphenyl diazonium borofluoride in nitrobenzene in the presence of copper. In 250 g (2 M) of nitrobenzene at 28° during two hours, with mixing by a stirrer, was placed, alternately, 111 g (0.5 M) of para-methoxyphenyl diazonium borofluoride and 50 g of copper powder. Stirring was continued for 20 days at 60° and for 10 days at 90°, after which, reaction for diazonium compounds with β -naphthol was negative. The precipitate of tar and copper was filtered off. This precipitate after treatment with 10% sodium hydroxide solution and distillation with superheated steam (bath temperature 220°) gave 0.03 g of yellow crystals; after two crystallizations from methanol, m.p. 64-75°. According to optical analysis (solvent isooctane, $\nu_{\max} = 38,500 \text{ cm}^{-1}$, $\nu_{\min} = 33,000 \text{ cm}^{-1}$) the product was chiefly 4-methoxy-3'-nitrodiphenyl ($\nu_{\max} = 38,500 \text{ cm}^{-1}$; $\nu_{\min} = 33,000 \text{ cm}^{-1}$).

The filtrate from the precipitate of copper and tar was washed with 10% sodium hydroxide solution and distilled with superheated steam (bath temperature 240°). The last drops of the distillate crystallized; after two crystallizations from methanol, red crystals with decomposition point 218-219°, containing nitrogen, were obtained. They were evidently 4,4'-dihydroxyazobenzene. According to the literature data [2], m.p. 216-218°.

The main quantity of the distillate was extracted with ether, dried with sodium sulfate, and after distillation of the ether and nitrobenzene, distilled in a vacuum: fraction I with b.p. 150-175° (2 mm), 3.71 g; fraction II with b.p. 175-180° (2 mm), 5.4 g; fraction III with b.p. 185-190° (2 mm), 0.12 g. From fractions I and II we isolated crystals, after separation by crystallization from methanol, which melted at 82° and gave no melting point depression with 4-methoxy-3'-nitrodiphenyl. Combined together the total weight was 2.6 g. The filtrate from the crystals from fractions I and II from optical analysis ($\nu_{\max} = 42,000 \text{ cm}^{-1}$) was the ortho-isomer (2-nitro-4'-methoxydiphenyl has $\nu_{\max} = 42,000 \text{ cm}^{-1}$), weight 6.5 g. Fraction III crystallized and after crystallization from methanol, the melting point and mixed melting point with 4-methoxy-4'-nitrodiphenyl was 107-108°, weight 0.12 g.

Decomposition of para-chlorophenyl diazonium borofluoride in nitrobenzene in the presence of copper. In 150 g of nitrobenzene we placed at 50°, 65 g of para-chlorophenyl diazonium borofluoride and 50 g of copper. Stirring of the reaction mixture was continued for 16 days at 50° and 5 days at 70°, after which the reaction mixture gave a negative test for diazonium compounds (β -naphthol). The precipitate of tar and copper was filtered off and washed with benzene, 10% sodium hydroxide solution, and was distilled with superheated steam (bath temperature 220°). The first part of the distillate (liquid) was added to the filtrate from the tar and copper. Then the orange crystals which distilled over (4.3 g) were crystallized from methanol and acetone and melted at 180-182°. Found: C 57.65; 57.44; H 3.50; 3.50%. $\text{C}_6\text{H}_4\text{NCl}$. Calculated: C 57.30; H 3.21%. According to the literature data [3,4], 4,4'-dichloroazobenzene melts at 183-184°.

The filtrate from the tar and copper, after the usual washing with alkali solution and water and distillation of the benzene and nitrobenzene, was distilled with superheated steam (bath temperature 240°). At first a liquid distilled over, then light crystals and then somewhat darker ones collected separately. To the liquid portion was added the ether extract of the watery distillate, dried with calcium chloride, and after distillation of the solvent it was vacuum distilled; we obtained 2.2 g of a semiliquid mass, b.p. 110-115° (2 mm). The absorption curve in the ultraviolet (solvent, isooctane, $\nu_{\max} = 42,500 \text{ cm}^{-1}$) resembled the absorption curve of 4-chloro-2'-nitrodiphenyl ($\nu_{\max} = 42,500 \text{ cm}^{-1}$). The light crystals which distilled with steam, after recrystallization from heptane, melted at 100-127°, weight 0.2 g, and without further crystallization they were submitted to optical analysis (in isooctane: $\nu_{\max} = 33,800 \text{ cm}^{-1}$ and $\nu''_{\max} = 40,000 \text{ cm}^{-1}$), that is, these crystals contained 4-chloro-4'-nitrodiphenyl ($\nu_{\max} = 33,800 \text{ cm}^{-1}$) and 4-chloro-3'-nitrodiphenyl ($\nu_{\max} = 40,000 \text{ cm}^{-1}$). The fraction of darker crystals, 0.38 g, had $\nu_{\max} = 33,800 \text{ cm}^{-1}$ and $\nu''_{\max} = 42,500 \text{ cm}^{-1}$, that is, they had a spectrum like that of 4-chloro-4'-nitrodiphenyl and 4-chloro-2'-nitrodiphenyl. In the crystallization of both fractions a further 4.2 g of crystals of 4,4'-dichloroazobenzene, m.p. 180-182°, separated.

Decomposition of ortho-carbomethoxyphenyl diazonium borofluoride in nitrobenzene in the presence of copper.

The experiments were carried out under conditions analogous to the preceding: nitrobenzene 200 g, diazonium borofluoride 100 g, copper 57 g. The temperature for adding the diazonium salt and copper was 24°, duration of addition, about one hour. The mixture was kept for 30 days at room temperature; the precipitate of tar and copper was filtered off. From the precipitate after the usual treatment with alkali solution and distillation with superheated steam and fractionation in a vacuum we obtained the fractions: fraction I with b.p. 147-170° (4 mm), several drops; fraction II with b.p. 170-186° (4 mm), several drops. On cooling, fraction I gave a small quantity of crystals with m.p. 74-78° which gave no melting point depression with 2-carbomethoxy-4'-nitrodiphenyl. All of fraction I had $\nu_{\max} = 36,000 \text{ cm}^{-1}$ (2-carbomethoxy-4'-nitrodiphenyl, $\nu_{\max} = 36,000 \text{ cm}^{-1}$), from $\nu_{\max} = 40,000 \text{ cm}^{-1}$ the form of the curve was analogous to the form for 2-carbomethoxy-2'-nitrodiphenyl (has no maximum or minimum). Fraction II on cooling and dilution with ethyl alcohol by spectroscopy in the ultraviolet had a curve analogous to that for 2-carbomethoxy-2'-nitrodiphenyl.

From the filtrate of the precipitate of tar and copper after the usual treatment with aqueous alkali, distillation with superheated steam, and distillation of the nitrobenzene, after two vacuum distillations (b.p. 175-180° at 2 mm) we obtained 3.8 g of a crystalline substance. After crystallization from heptane and alcohol, m.p. 72°, $\nu_{\max} = 35,500 \text{ cm}^{-1}$. Found: C 70.54; H 5.17; 5.24%. $\text{C}_8\text{H}_7\text{O}_2$. Calculated: C 71.10; H 5.22%.

From the literature [4] for the dimethyl ester of diphenic acid, m.p. 73.5°.

After saponification with 10% aqueous alcoholic solution of KOH, the ester gave diphenic acid, crystallized from water, m.p. 222°. According to the literature [4], the melting point of diphenic acid is 228°. Found: C 69.80; 69.62; H 4.20; 4.31%. $\text{C}_7\text{H}_5\text{O}_2$. Calculated: C 69.42; H 4.16%.

Decomposition of para-carbomethoxyphenyl diazonium borofluoride in nitrobenzene in the presence of copper.

The experiment was carried out like the previous ones: nitrobenzene 210 g, para-carbomethoxyphenyl diazonium borofluoride 111 g, copper powder 56 g, initial temperature 40-50°. We stirred for two weeks at 70-80°. The precipitate of tar and copper was filtered and washed with benzene. The combined filtrates were washed with 10% NaOH solution, the benzene and nitrobenzene were distilled off, the residue was distilled with superheated steam (bath temperature 240°) and then in a vacuum: b.p. 230-235° (10 mm), 2.6 g. The residue partly crystallized. After crystallization from heptane the m.p. and mixed m.p. with 2-nitro-4'-carbomethoxydiphenyl was 71-72°. Distillation with superheated steam (bath temperature 240°) of the precipitate of tar and copper gave two types of crystals: orange and colorless. The latter were separated from the orange crystals by sublimation. The sublimed colorless crystals melted at 179-180° and dissolved in alkali; acid to litmus. Found: C 59.75, 59.77; H 3.70, 3.79%. $\text{C}_7\text{H}_5\text{O}_2$. Calculated: C 60.00; H 3.60%. According to the literature [5] para-fluorobenzoic acid melts at 181-182°.

The residue after separation of the sublimate of para-fluorobenzoic acid was red and after crystallization from heptane melted at 143°. Found: C 66.25; 66.31; H 5.59; 5.44%. $\text{C}_9\text{H}_9\text{O}_2\text{N}$. Calculated: C 66.24; H 5.52%. According to the literature [6] the diethyl ester of azobenzene-4,4'-dicarboxylic acid melts at 145.5°.

The distillate from distillation of the precipitate of tar and copper, separated from the crystals of para-fluorobenzoic acid and azo compound, was extracted with ether and dried over calcium chloride. After distillation of the ether and nitrobenzene there remained 6.9 g of a yellow semicrystalline precipitate. The crystals were filtered with suction and by crystallization and sublimation were separated from some remaining para-fluorobenzoic acid and azo compound. The crude filtrate had an absorption spectrum curve with $\nu_{\max} = 40,500 \text{ cm}^{-1}$ similar to that for 2-nitro-4'-carbomethoxydiphenyl ($\nu_{\max} = 41,000 \text{ cm}^{-1}$), but the ν_{\max} shifted toward the ν_{\max} for 3-nitro-4'-carbomethoxydiphenyl ($\nu_{\max} = 39,000 \text{ cm}^{-1}$). After distillation in a vacuum, b.p. 160-170° (3 mm). We obtained 1 g of crystalline precipitate. The m.p. and mixed m.p. with 3-nitro-4'-carbomethoxydiphenyl was 103-106°.

Decomposition of phenyl diazonium borofluoride in ethyl benzoate in the presence of copper. To a well stirred sample of 14 g of copper powder in 180 g of ethyl benzoate we added in small portions at room temperature in the course of two hours 76 g of phenyl diazonium borofluoride. The temperature after each addition rose to 32°, but decomposition took place slowly. We added 14 g more of copper and continued to stir for two days (stopping at night) at 60° and one day at 80°. After this the reaction for diazonium compounds in the reaction mixture was negative. The reaction mixture was dissolved in ether, filtered from the copper, washed with 10% sodium hydroxide, with water, and dried over calcium chloride. After distilling off the ether and most of the ethyl benzoate we fractionated in a vacuum: fraction I with b.p. 130-152° (2 mm), 3.6 g; fraction II with b.p. 152-210° (2 mm), 3.1 g.

Each fraction was separately saponified by boiling for three hours with 20 ml of 20% potassium hydroxide solution in methyl alcohol. After distillation of the alcohol and acidification with hydrochloric acid we added soda to an alkaline reaction and distilled with steam. In both experiments reaction for phenol in the distillate with ferric chloride or with bromine water was negative. To the residue from the steam distillation we added 3 ml of 10% sodium hydroxide solution, diluted with water. From fraction II in the experiment the precipitate insoluble in alkali was filtered off, heated for 15 minutes with concentrated hydrochloric acid, and the resulting needles, 0.36 g, were recrystallized from ethyl alcohol. The m.p. and mixed m.p. with para-diphenyl carboxylic acid was 222°. Acidification of the alkaline filtrate gave a precipitate which melted after sublimation at 121°; a mixed m.p. with benzoic acid was 121°.

From fraction III in the experiment the alkali insoluble precipitate after similar treatment gave 0.43 g of para-diphenyl carboxylic acid with m.p. 220°. The semisolid precipitate formed by acidifying the alkaline filtrate with hydrochloric acid was extracted with ether, the ether solution was dried with sodium sulfate, the ether was distilled off, and the residue was fractionally crystallized from heptane. We obtained 0.2 g of substance with a m.p. and mixed m.p. with known metadiphenyl carboxylic acid of 159-160°, and 0.35 g of benzoic acid with m.p. and mixed m.p. of 121°. For carrying out theoretical measurements the authors express thanks to I. Ya. Kachkurova.

SUMMARY

In the presence of copper powder the decomposition of aryl diazonium borofluorides in nitrobenzene and ethyl benzoate gives products of homolytic splitting of the diazonium salts. The synthesis of metalloorganic compounds from diazonium salts in the presence of metals occurs by a homolytic mechanism.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

ESTERS OF β -KETOPHOSPHONIC ACIDS. VII.
 THE PRODUCTS OF THE REACTION
 OF α -CHLOROCYCLOHEXANONE WITH THE DIETHYL ESTER
 OF ETHYLPHOSPHONOUS ACID AND THE SODIUM SALT
 OF THE MONOETHYL ESTER OF ETHYLPHOSPHONOUS ACID

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In previous studies of the action of α -halocarbonyl compounds with triethyl phosphite and sodium diethylphosphite [1] we have investigated the reaction between α -chlorocyclohexanone and the diethyl ester of ethylphosphonous acid and sodium monoethyl ethylphosphonite. By the action of α -chlorocyclohexanone on diethyl ethylphosphonite [2] we isolated a good yield of a substance with b.p. 85-86° (0.5 mm); d_4^{20} 1.0709; n_D^{20} 1.4642. Found: MR 56.26. $C_{10}H_{19}O_3P$ F. Calculated MR 56.49*.

By titration of the product with perphthalic acid we obtained 150% unsaturation, calculated on one double bond** The high unsaturation can be explained by a deeper oxidation of the cyclohexanone ring by the perphthalic acid. It is known from sources in the literature that perbenzoic acid oxidizes cyclohexanone and cyclopentanone to the corresponding lactones [3]. Reesterification of the product with ethyl alcohol leads to cyclohexanone and the diethyl ester of ethylphosphonic acid. In the reaction of 2,4-dinitrophenylhydrazine we obtained the 2,4-dinitrophenylhydrazone of cyclohexanone.

The combination scattering spectrum of the product of the reaction between α -chlorocyclohexanone and the diethyl ester of ethylphosphonous acid had the following frequencies:

($\Delta\nu$, cm^{-1}) 243(2d), 280(2d), 316(1), 384(0), 439(1d), 529(1d), 608(1), 627(2), 705(5b), 742(1), 770(3), 801(2), 837(3), 849(2), 896(1), 925(3), 985(3), 1048(4), 1078(3), 1100(3), 1138(1), 1176(3), 1237(2), 1267(4), 1299(2), 1338(2), 1370(1), 1409(2), 1434(8), 1454(5), 1683(6), 2657(0), 2717(0), 2843(6), 2863(3d), 2885(4d), 2931(5b, db), 2977(3), 3024(1), 3064(2).

The product of the reaction of α -chlorocyclohexanone with sodium monoethyl ethylphosphonite [4] had b.p. 91-93° (0.5 mm); d_4^{20} 1.0793; n_D^{20} 1.4665; Found: MR 55.99 and differed somewhat in its constants from the product obtained in the reaction of α -chlorocyclohexanone with the diethyl ester of ethylphosphonous acid.

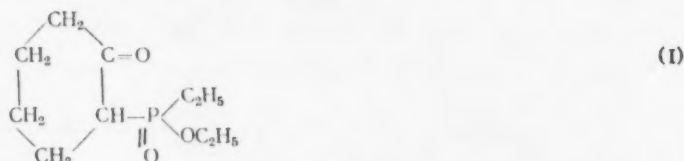
In reesterification by ethyl alcohol we obtained cyclohexanone and ethyl ethylphosphonate. With 2,4-dinitrophenylhydrazine we obtained cyclohexanone 2,4-dinitrophenylhydrazone. Titration with perphthalic acid gave 100% unsaturation, calculated on one double bond. The combination scattering spectrum of the product with b.p. 91-93° (0.5 mm) showed the following frequencies:

($\Delta\nu$, cm^{-1}) 244(2d), 277(2d), 318(2d), 380(2d), 439(2d), 492(2), 528(2), 598(2b), 626(2), 656(3), 706(3b), 742(1), 768(3), 806(0), 836(3), 850(1), 896(1), 926(3), 984(3), 1046(4), 1078(3), 1100(3), 1137(1), 1176(4), 1235(2), 1266(5), 1296(3), 1339(2), 1371(2), 1410(2), 1435(6), 1455(4), 1627(1), 1683(4), 2658(3), 2717(2), 2746(1), 2775(1), 2843(4), 2887(3b), 2938(8b), 2981(4d), 3025(1), 3066(3).

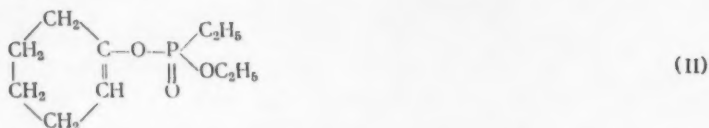
*For the ethyl ester of ethylcyclohexanon-2-yl 1-phosphonic acid [1], MR_D is calculated as 55.93.

**A similar picture was obtained by perphthalic acid titration of the product of reaction of α -chlorocyclohexanone with triethyl phosphite, where we obtained 170% unsaturation [1].

Comparing the combination scattering spectra of the products of reaction of α -chlorocyclohexanone with diethyl ethylphosphonite and with sodium monoethyl ethylphosphonite shows a great similarity in their frequencies. The spectra do not contain the frequencies of the carbonyl group, but have frequencies 1684 and 1683 cm^{-1} , respectively. According to the literature, the spectra of 1-methylcyclohexene [5], carbomenthene [6], and other 1-substituted derivatives of cyclohexene have combination frequencies of the valence oscillation group $\text{C}=\text{C}$ at about 1680 cm^{-1} , close to that which we found. The absence in the spectra of frequencies of the carbonyl group shows that in the reaction there is no formation of the ethyl ester of ethylcyclohexanon-2-yl 1-phosphonic acid (I):



Obtaining a mixed cyclohexen-1-yl 1-diethylphosphate in the reaction of α -chlorocyclohexanone with triethyl phosphite [1] and the presence in the spectra of the products of the characteristic frequency of 1684 cm^{-1} for the unsaturated bond $\text{C}=\text{C}$ suggests that in the action on α -chlorocyclohexanone of diethylethylphosphonite there is formed a mixed cyclohexen-1-yl 1-ethyl ester of ethylphosphonic acid (II). Ester (II) is also formed in the reaction of α -chlorocyclohexanone with sodium monethyl ethylphosphonous acid:



The ultraviolet spectra of the products are given in Fig. 1. According to the ultraviolet spectra there is also difference in the products of reaction of α -chlorocyclohexanone with diethyl ethylphosphonite and with sodium monoethyl ethylphosphonite. From the character of the absorption in solutions in methyl alcohol (see fig., curve 1) the product obtained with diethyl ethylphosphonite has more similarity with the absorption of ethyl isopropenyl ethylphosphonate [7]. In the solution in methyl alcohol containing sodium methylate (fig., curve 2) we find a clear maximum at 2800 \AA , which can be due to absorption by cyclohexanone formed in the alcoholysis of cyclohexen-1-yl 1-ethyl ester of ethylphosphonic acid (II) in an alkaline medium.

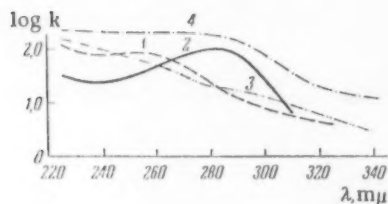


Fig. 1. Ultraviolet absorption spectra. 1) Cyclohexen-1-yl 1-ethylester of ethylphosphonic acid in CH_3OH ; 2) the same in $\text{CH}_3\text{OH} + \text{CH}_3\text{ONa}$; 3) product with b.p. $91-93^\circ$ (0.5 mm) in CH_3OH ; 4) the same in $\text{CH}_3\text{OH} + \text{CH}_3\text{ONa}$.

The absorption curve (fig., curve 3) for the product with b.p. $91-93^\circ$ (0.5 mm) in a methyl alcohol solution has a flatter character. On addition of sodium methylate to the solution there is a marked rise in absorption in the region of 2800 \AA (curve 4). The absence of a sharp maximum at 2800 \AA can evidently be explained by the presence of impurities. It is quite possible that this absorption is produced by the presence of the ethyl ester of ethyl-1,2-epoxycyclohexyl-1-phosphonic acid (III) since the change in absorption in an alkaline medium is fully analogous to the change in absorption of the ethyl ester of ethylepoxyisopropylphosphonic acid under different conditions [7]:



As this material indicates, the reaction between the diethyl ester of ethylphosphonous acid or sodium monoethyl ethylphosphonite on the one hand, and α -chlorocyclohexanone on the other, goes in the same way as in the case of triethylphosphite and sodium diethyl phosphite.

EXPERIMENTAL

Action of diethyl ethylphosphonite on α -chlorocyclohexanone. The experiment was carried out under conditions described for chloroacetone [7]. To 15 g of chlorocyclohexanone was added dropwise 16.9 g of diethyl ethylphosphonite. The addition of the ester was carried out at such a rate that the temperature in the flask was kept at 65-80°. After heating for 30 minutes at 80-100° the reaction product was distilled. We obtained a fraction weighing 16.6 g (67.7% of the theory) with the following constants: b.p. 85-86° (0.5 mm), d_4^{20} 1.0709; n_D^{20} 1.4642. Found: P 14.21%; MR 56.26. $C_{10}H_{19}O_3PF$. Calculated: P 14.22%; MR 56.49.

Reesterification with ethyl alcohol (10 ml) in the presence of sodium ethylate (0.1 g Na) of the product with b.p. 85-86° (0.5 mm) was carried out by heating for two hours on a water bath. It was neutralized with glacial acetic acid. Fractionation gave cyclohexanone (1.2 g) (we obtained the 2,4-dinitrophenylhydrazone with m.p. 158-159°), and the diethyl ester of ethyl phosphonic acid (2 g), 78-80° (9 mm), d_4^{20} 1.0216, n_D^{20} 1.4170.

Action of sodium monoethyl ethylphosphonite on α -chlorocyclohexanone. In a flask fitted with a stirrer, dropping funnel, and reflux condenser was placed 17.4 g of α -chlorocyclohexanone in ether, and we added an ether solution of the sodium derivative prepared from 16 g of ethyl ethylphosphonite in 150 ml of ether. After further heating on a water bath for an hour and a half, separation of the precipitated sodium chloride, and distillation of the ether, the residue was fractionated with a Widmer column. We isolated 11.3 g of product, or 39.5% of the theory, with the following constants: b.p. 91-93° (0.5 mm), d_4^{20} 1.0793; n_D^{20} 1.4665. Found: P 14.17%; MR 55.99. $C_{10}H_{19}O_3PF$. Calculated: P 14.22%; MR 56.49.

Reesterification with ethyl alcohol was carried out as described above. We took 4 g of product and obtained in the fractionation: cyclohexanone (dinitrophenylhydrazone m.p. 158-159°) and diethyl ethylphosphonate (b.p. 53-55° at 2 mm); d_4^{20} 1.0284; n_D^{20} 1.4160.

The combination scattering spectra were obtained on a three prism ISP-51 spectrograph with the excited mercury lines 4358 and 4047 Å; the ultraviolet absorption spectra were obtained with a quartz SF-4 spectrophotometer.

SUMMARY

The action of diethyl ethylphosphonite on α -chlorocyclohexanone gives cyclohexen-1-yl-1-ethyl ethylphosphonate. Cyclohexen-1-yl-1-ethyl ethylphosphonate is also obtained by the action of sodium monoethyl ethylphosphonite on α -chlorocyclohexanone.

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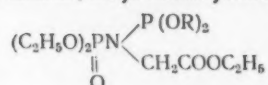
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2. B. A. Arbuzov and N. I. Rizpolozhenskii, *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk*, 854 (1952).
3. S. L. Friess, *J. Amer. Chem. Soc.*, **71**, 2571 (1949).
4. B. A. Arbuzov and N. I. Rizpolozhenskii, *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk*, 956 (1952); 253 (1955).
5. C. Chiurdoglu, A. Guillemonat, *Bull. Soc. Chim. France*, **5**, 1624 (1938).
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THE SYNTHESIS AND PROPERTIES OF SOME DI-N-SUBSTITUTED AMIDOPHOSPHATES

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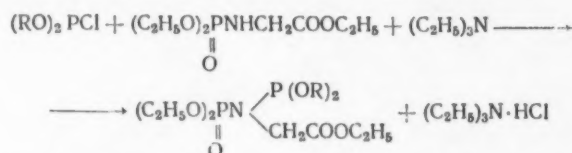
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No.11,
pp. 1985-1990, November 1960
Original article submitted June 11, 1959.

In a previous communication [1] we reported physiologically active di-N- substituted amidoesters of phosphoric acid in which one of the substituents of an amide group hydrogen was alkyl or aryl, and the substituent of the second was some sort of organic phosphorus derivative. In the present work, which is a continuation of this study, we have carried out the synthesis of di-N-substituted amides of phosphoric acid which contain in the amide group, along with the organic phosphorus residue, a hydrocarbon radical, ethyl carboxymethyl, that is, compounds of the type



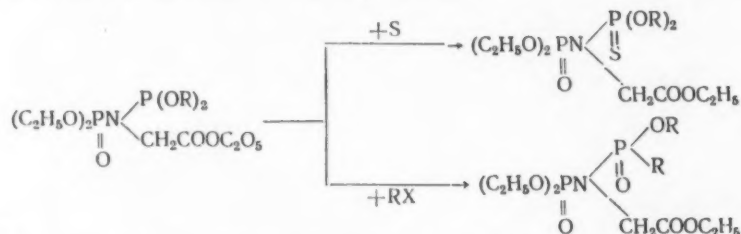
These organic phosphorus derivatives can also be active physiologically, since they belong to the above type of substituted amides and also contain on the nitrogen the radical $\text{CH}_2\text{COOC}_2\text{H}_5$ which occurs in the composition of some organic phosphorus compounds with biological activity (for example, N-substituted amidophosphates, mixed esters of thiophosphoric acid.).

Di-N-substituted amidophosphates were obtained by the action of acid chlorides of dialkylphosphorous acid on the N-ethylcarboxymethylamide of diethylphosphoric acid according to the scheme:



The reaction takes place at room temperature in ether solution. Judging by the amount of triethylamine hydrochloride formed in the reaction, the reaction is almost complete, but evidently the main reaction is complicated by side processes which lower the yield of product.

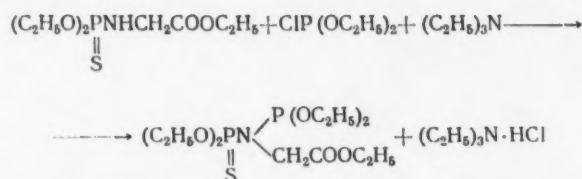
Since di-N- substituted amidophosphates contain trivalent phosphorus bound with ester groups, they can obviously give the characteristic reactions of esters of phosphorous acid, that is, they can bind sulfur, and isomerize into an ester of alkylphosphonic acid under the influence of alkyl halides



Some difficulties were encountered in carrying out the isomerization process. It was shown that this reaction occurs only in the case of those derivatives which have the lower hydrocarbon radicals in the ester groups on the trivalent phosphorus. Beginning with the propyl radical, probably because of spacial difficulties, isomerization of the substances does not occur even on raising the temperature and using active alkyl iodides. Acid chlorides of diethyl-

phosphoric acid, which are less active than the corresponding acid chlorides of acids of trivalent phosphorus, do not react at all under the above described conditions with the N-ethylcarboxymethyl amide of diethylphosphoric acid. We used benzene as the solvent, but in this case reaction did not take place even with lengthening of the boiling. Without a solvent the reaction of the substances partly occurs, but isolation of the reaction product in pure form did not succeed because the boiling points of the initial and synthesized substances were close to each other.

Using as the starting monosubstituted amide N-ethylcarboxymethylamide of diethylthiophosphoric acid, and acting on it with diethylphosphorous acid chloride, we obtained the completely N-substituted amidothiophosphate

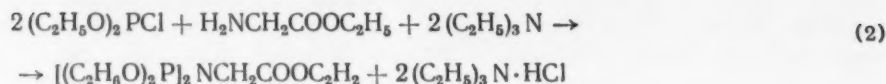
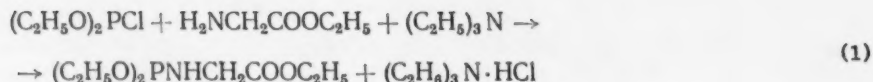


These reactions occur under more severe conditions than for the corresponding monosubstituted amides of diethylphosphoric acid. Sulfur adds to the trivalent phosphorus of the amidothiophosphates with difficulty and incompletely. Attempts to isomerize the product of the reaction with ethyl iodide were unsuccessful. The substance began to decompose even when heated with the alkyl halide, and finally decomposed on distillation.

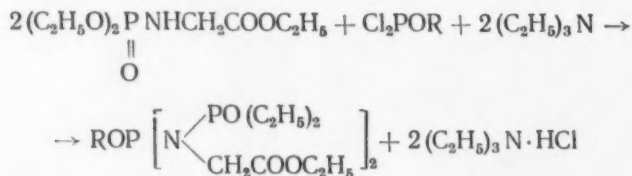
TABLE

No.	Formula	B.p. P, mm Hg	n_D^{20}	d_4^{20}	MR		P content, %		Yield, %
					found	calc.	found	calc.	
I	$(\text{C}_2\text{H}_5\text{O})_2\text{PN} \begin{array}{l} \text{P}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{O} \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	120—121 (0,5)	1,4470	1,1338	84,60	84,88	17,52 17,53	17,27	35,84
II	$(\text{C}_2\text{H}_5\text{O})_2\text{PN} \begin{array}{l} \text{P}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{O} \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	132—134 (1)	1,4430	1,1008	93,19	93,09	15,67 15,84	16,02	53,1
III	$(\text{C}_2\text{H}_5\text{O})_2\text{PN} \begin{array}{l} \text{P}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{O} \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	146—148 (1)	1,4455	1,1076	93,05	93,09	16,04 15,80	16,02	50,0
IV	$(\text{C}_2\text{H}_5\text{O})_2\text{PN} \begin{array}{l} \text{P}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{S} \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	140, 143, 5 (1)	1,4705	1,1441	91,53	91,40	16,51 16,67	16,53	36,3
V	$\text{C}_2\text{H}_5\text{OP} \left[\text{N} \begin{array}{l} \text{PO}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array} \right]_2$	215—217 (2)	1,4575	1,2010	125,3	124,73	17,01 16,98	16,85	20,5
VI	$i\text{-C}_3\text{H}_7\text{OP} \left[\text{N} \begin{array}{l} \text{PO}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array} \right]_2$	—	1,4485	1,1722	129,32	129,4	16,55 16,36	16,43	96,6
VII	$(\text{C}_2\text{H}_5\text{O})_2\text{PNHCH}_2\text{COOC}_2\text{H}_5$	85—86 (2)	1,4442	1,0575	56,01	56,064	13,93 13,86	13,9	34,6
VIII	$[(\text{C}_2\text{H}_5\text{O})_2\text{PNHCH}_2\text{COOC}_2\text{H}_5]$	110—115 (1)	1,4520	1,0910	84,52	85,03	17,64 17,65	18,07	29
IX	$(\text{C}_2\text{H}_5\text{O})_2\text{PN} \begin{array}{l} \text{P}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{O} \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	152—153 (1)	1,4420	1,1658	81,51	81,66	16,94 17,00	17,27	74,7
X	$(\text{C}_2\text{H}_5\text{O})_2\text{PN} \begin{array}{l} \text{P}(\text{OC}_2\text{H}_5)_2 \\ \parallel \\ \text{O} \\ \text{CH}_2\text{COOC}_2\text{H}_5 \end{array}$	152—154 (1)	1,4570	1,1434	99,80	99,52	14,65 14,58	14,79	62,36
XI	$[(\text{C}_2\text{H}_5\text{O})_2\text{P}]_2\text{NCH}_2\text{COOC}_2\text{H}_5$	156—157 (1)	1,4835	1,1807	98,52	97,7	15,55 15,72	15,23	44,61

In the action of the acid chloride of diethylphosphorous acid on ethyl glycinate we obtained mono- and di-N-substituted amides of diethylphosphorous acid:



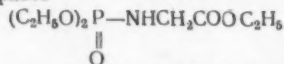
In the reaction of alkoxydichlorophosphites with N-ethyl-carboxymethylamide of diethylphosphoric acid there is formed a derivative with three atoms of phosphorus



The formulas of all the compounds synthesized, their physical constants, and yields are given in the table.

EXPERIMENTAL

Action of diisopropylchlorophosphite on N-ethylcarboxymethyl amide of diethylphosphoric acid (II). To a solution of 21.51 g (0.09 M) of the amidophosphate



(b.p. 135-136° at 1 mm) and 10.1 g (0.1 M) of triethylamine $(\text{C}_2\text{H}_5)_3\text{N}$ in 60 ml of dry ether was added 16.6 g (0.09 M) of diisopropyl phosphorous acid chloride $(\text{iso-C}_3\text{H}_7\text{O})_2\text{PCl}$. After addition of the acid chloride the reaction mixture was stirred for four hours at room temperature. We obtained 12 g (97%) of triethylamine hydrochloride $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HCl}$ and 36.1 g of crude product after removal of the solvent. It was fractionated from an Arbuzov flask at 1 mm. We obtained: fraction I, b.p. 48-124°, 3 g; fraction II, b.p. 124-139°, 27.8 g; residue, 1.5 g.

On distillation of fraction II we obtained 18.5 g (53.1% of the theory) of a substance with b.p. 132-134° (1 mm), n_D^{20} 1.4430; d_4^{20} 1.1008. Found: P 15.67; 15.84%; MR 93.19. $\text{C}_{14}\text{H}_{31}\text{O}_7\text{P}_2\text{N}$. Calculated P 16.02%; MR 93.09. Under analogous conditions we obtained compounds (I) and (III), shown in the table.

Action of diethylchlorophosphite on N-ethylcarboxymethylamide of diethylthiophosphoric acid (IV). A mixture of 20.4 g (0.08 M) of amidothiophosphate $(\text{C}_2\text{H}_5\text{O})_2\text{PNHCH}_2\text{COOC}_2\text{H}_5$ (b.p. 130-131° at 2 mm), 8.2 g (0.08 M) of tri-



ethylamine $(\text{C}_2\text{H}_5)_3\text{N}$, and 12.5 g (0.08 M) of the acid chloride $(\text{C}_2\text{H}_5\text{O})_2\text{PCl}$ in benzene solution was heated to weak boiling of the solvent and stirred for six hours. We obtained 9.1 g (83%) of amine salt $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HCl}$ and 25.8 g (86%) of crude product. After two distillations we isolated a main fraction with b.p. 140-143.5° (1 mm); yield 10.9 g (36.3%), n_D^{20} 1.4705; d_4^{20} 1.1441. Found: P 16.51; 76.67; S 8.51 8.52%; MR 91.53. $\text{C}_{12}\text{H}_{27}\text{O}_6\text{P}_2\text{NS}$. Calculated: P 16.53; S 8.53%; MR 91.40.

Action of ethyldichlorophosphite on N-ethylcarboxymethylamide of diethyl phosphoric acid (V). Ethyldichlorophosphite, $\text{C}_2\text{H}_5\text{OPCl}_2$, 5.3 g (0.036 M) was added by drops from a dropping funnel to an ether solution of the amidophosphate, $(\text{C}_2\text{H}_5\text{O})_2\text{P}(=\text{O})\text{NHCH}_2\text{COOC}_2\text{H}_5$, 17.2 g (0.072 M) (b.p. 133-134° at 1 mm) and triethylamine, 7.8 g (0.077 M) with cooling of the flask by ice water. Then the mass was stirred at room temperature for four hours. We obtained 9.4 g (95%) of the amine salt $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{HCl}$ and 18.6 g (93%) of the crude product in the form of a thick, light yellow liquid. Fractionation was carried out from an Arbuzov flask at 2 mm. We obtained: fraction I, b.p. 135-206°, 6.25 g; fraction II, b.p. 206-215°, 1.5 g; fraction III, b.p. 215-217°. The yield of fraction III with b.p. 215-217° (2 mm) was 4.08 g (20.5% of the theory), n_D^{20} 1.4575; d_4^{20} 1.201. Found: P 17.01; 16.98%; MR 125.3. $\text{C}_{18}\text{H}_{39}\text{O}_{11}\text{P}_3\text{N}_2$. Calculated: P 16.85%; MR 124.73. The substance was soluble in water and most of the usual organic solvents. In an analogous way we synthesized the organic phosphorus derivative (VI). Since this substance decomposed on distillation, its physical constants, yield, and results of analysis are given for the technical product.

Action of diethylphosphorous acid chloride on ethyl glycinate (VII). Diethylphosphorous acid chloride $(\text{C}_2\text{H}_5\text{O})_2\text{PCl}$, 15.18 g (0.097 M) (b.p. 74-75° at 60 mm) was added to a solution of ethyl glycinate $\text{NH}_2\text{CH}_2\text{COOC}_2\text{H}_5$, 10 g (0.097 M)

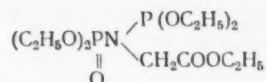
and triethylamine ($\text{C}_2\text{H}_5)_3\text{N}$, 11 g (0.108 M) in ether. After adding the acid chloride we stirred the mass for three hours at room temperature. We obtained 12 g (90%) of the amine salt ($\text{C}_2\text{H}_5)_3\text{N}\cdot\text{HCl}$. The residue after removal of the solvent was fractionated at 2 mm. We obtained: fraction I, b.p. 45-80°, 3 g; fraction II, b.p. 80-100°, 11.3 g; fraction III, b.p. 100-140°, 2.3 g; residue 2 g. When fraction II was fractionated it gave 7.5 g (34.6%) of substance with b.p. 85-86° (2 mm), n_D^{20} 1.4442; d_4^{20} 1.0575. Found: P 13.93; 13.86%; MR 56.01. $\text{C}_8\text{H}_{18}\text{O}_4\text{PN}$. Calculated P 13.90%; MR 56.064.

Obtaining n-ethylcarboxymethylamide of diethylphosphorous acid (VIII). To a solution of ethyl glycinate $\text{NH}_2\text{CH}_2\text{COOC}_2\text{H}_5$, 5.25 g (0.051 M) and triethylamine, 11 g (0.108 M) in ether was added diethylphosphorous acid chloride ($\text{C}_2\text{H}_5\text{O})_2\text{PCl}$, 15.96 g (0.102 M) (b.p. 74-75° at 60 mm), cooling the flask with ice water. Then the mass was stirred for four hours at room temperature. We obtained 12.2 g (86.2%) of amine salt ($\text{C}_2\text{H}_5)_3\text{N}\cdot\text{HCl}$. The residue after removal of the triethylamine hydrochloride and solvent was fractionated at 1 mm. We obtained: fraction I, b.p. 52-92°, 1.6 g; fraction II, b.p. 92-132°, 11.02 g; residue 2.5 g.

From fraction II by fractionation we isolated a substance with b.p. 110-115° (1 mm), 5.2 g (29%), n_D^{20} 1.4520; d_4^{20} 1.0910. Found: P 17.64; 17.65%; MR 84.52. $\text{C}_{12}\text{H}_{27}\text{O}_5\text{P}_2\text{N}$. Calculated: P 18.07%; MR 85.03.

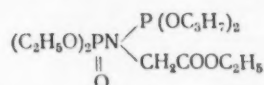
Reactions of Di-N-Substituted Amidophosphates

Isomerization of N-ethylcarboxymethylamide of diethylphosphoric and diethylphosphorous acids by ethyl iodide (IX). We sealed 8.3 g of the amidophosphate



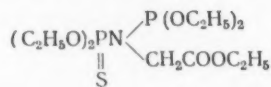
(b.p. 120-121° at 0.5 mm) and 1 ml of ethyl iodide in a glass tube and heated for four hours at 135-140°. By fractionation we obtained 6.2 g (74.7%) of substance with b.p. 152-153° (1 mm), n_D^{20} 1.4420; d_4^{20} 1.1658. Found: P 16.94; 17.00%; MR 81.51. $\text{C}_{12}\text{H}_{27}\text{O}_7\text{P}_2\text{N}$. Calculated: P 17.27%.

Isomerization of N-ethylcarboxymethylamide of diethylphosphoric and dipropylphosphorous acids by propyl iodide. We heated 5.6 g of the amidophosphate



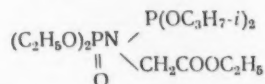
(b.p. 146-148° at 1 mm); n_D^{20} 1.4455 and 1 ml of propyl iodide in a sealed tube at 150-155° for five hours. On fractionation we obtained a fraction with b.p. 144-150° (1 mm); n_D^{20} 1.4425, yield 3.5 g (62.5%). Thus the isomerization reaction did not occur.

Isomerization of N-ethylcarboxymethylamide of diethylthiophosphoric and diethylphosphorous acids by ethyl iodide. We heated 1.8 g of the amidothiophosphate



and 1 ml of ethyl iodide in a sealed tube for four hours at 140-150°. The liquid darkened and evolved sulfur. The substance decomposed when distilled.

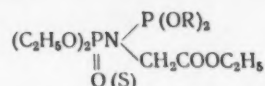
Addition of sulfur to N-ethylcarboxymethylamide of diethylphosphoric and diisopropylphosphorous acids (X). In a flask with a reflux condenser we placed 8 g (0.21 M) of the amide



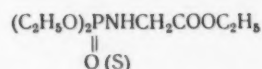
(b.p. 132-134° at 1 mm); n_D^{20} 1.4430) 0.67 g (0.021 g atom) of powdered sulfur, and 10 ml of dry benzene. The reaction mixture was heated in boiling benzene for three hours. On distillation we obtained 5.5 g (62.4%) of substance with b.p. 152-154° (1 mm); n_D^{20} 1.4570, d_4^{20} 1.1431. Found: P 14.65; 14.58%; MR 99.8. $\text{C}_{14}\text{H}_{31}\text{O}_7\text{P}_2\text{NS}$. Calculated: P 14.79%; MR 99.42. Under analogous conditions we obtained compound (XI).

SUMMARY

1. In the search for physiologically active compounds we have synthesized di-N-substituted amid(o)phosphates



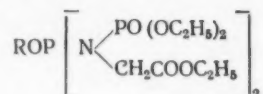
by the reaction of the corresponding dialkylchlorophosphites $(\text{RO})_2\text{PCl}$ with the N-ethylcarboxymethylamide of diethyl-(thio)phosphoric acids



2. We have studied the reaction of addition of sulfur to the resulting compounds and their isomerization into derivatives of alkylphosphonic acids under the influence of alkyl halides.

3. By the action of diethylphosphorous acid chloride on ethyl glycinate we have obtained mono- and disubstituted amides of diethylphosphorous acid $(\text{C}_2\text{H}_5\text{O})_2\text{PNHCH}_2\text{COOC}_2\text{H}_5$; $[(\text{C}_2\text{H}_5\text{O})_2\text{P}]_2\text{NCH}_2\text{COOC}_2\text{H}_5$.

4. By the reaction of alkoxydichlorophosphites with N-ethylcarboxymethylamides of diethylphosphoric acid we have synthesized derivatives with three atoms of phosphorus.



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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, and I. L. Knunyants

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Only trifluoromethyl and pentafluoropropyl derivatives are known among the fluorinated heteroorganic compounds of the fifth group. These were obtained by the homolytic reactions of perfluoromethyl iodide with elementary phosphorus and arsenic [1]. It was shown that in the absence of trifluoroiodomethane and pentafluoroiodopropane, perfluorovinyl halides did not form the corresponding derivatives of the elements under discussion but were changed into the products of cyclodimerization. Thus, on heating white phosphorus or arsenic with $\text{CF}_2=\text{CFI}$, $\text{CF}_2=\text{CFBr}$, or $\text{CF}_2=\text{CFCI}$ at 160° or higher the corresponding perfluorocyclobutene, 1,2-dibromo- and 1,2-dichlorocyclobutane were obtained. The formation of perfluorocyclobutene in the first case is the result of loss of iodine from the initially formed 1,2-diodohexafluorocyclobutane. The truth of the latter was established by the formation of perfluorocyclobutene on heating $\text{CF}_2=\text{CFI}$ at 200° .

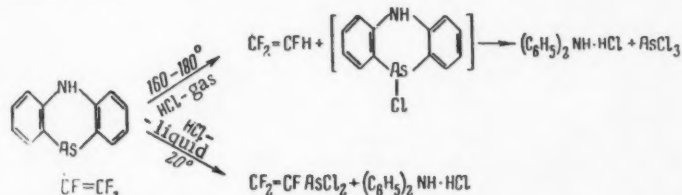
We have shown earlier that the corresponding Grignard reagents are easily formed from perfluorovinyl iodide and bromide [2] and these were used to introduce perfluorovinyl radicals onto carbon and silicon [2,3]. It seemed interesting to apply this method of perfluorovinylation to the preparation of perfluorovinyl derivatives of other elements, and in particular of phosphorus, arsenic, and antimony. The reaction of perfluorovinylmagnesium iodide with ethereal solutions of AsCl_3 , PCl_3 , SbCl_3 gave exclusively tertiary derivatives; tris-(trifluorovinyl)arsine, tris-(trifluorovinyl)phosphine, and tris-(trifluorovinyl)-stibine;



Primary and secondary derivatives were not obtained in this way. Attempts to prepare the latter by disproportionation between tris-(trifluorovinyl) derivatives and the halides of the corresponding elements were also not successful.

The synthesis of perfluorovinylchloroarsine was based on the fission of 10-alkyl-5, 10-dihydrophenarsine by dry hydrogen chloride, a known general method for alkylchloroarsines. The corresponding perfluorovinyl derivative of dihydrophenarsine was obtained by us in quantitative yield by the reaction of perfluorovinylmagnesium iodide with adamsite. However, decomposition of 10-perfluorovinyl-5, 10-dihydrophenarsine with dry hydrogen chloride at 160 – 180° led to the formation of arsenic trichloride, trifluoroethylene, and diphenylamine hydrochloride in consequence of the initial loss of a perfluorovinyl radical, which formed trifluoroethylene, and then fission of the phenarsine ring at the C-As bond.

It was shown [5] that tert-butyldichloroarsine was obtained in good yield by decomposition of the corresponding derivative of phenarsine with liquid hydrogen chloride. This method appeared suitable for the preparation of perfluorovinylchloroarsine, which was obtained by us in practically quantitative yield by the reaction of $\text{CF}_2=\text{CFA}(\text{C}_6\text{H}_4)_2\text{NH}$ with liquid hydrogen chloride. The preparation of primary and secondary perfluorovinylhalogenophosphenes was also carried out in a different way.



A number of authors have found that substituted amides of alkylphosphinic acids are easily cleaved by hydrogen chloride or hydrochloric acid with the formation of the corresponding acid chloride or the acid itself [6]. We have shown that analogous processes take place with a series of derivatives of trivalent phosphorus. On reacting the acid chloride of the tetraethyldiamide of phosphorous acid and the tetraethyldiamide of ethylphosphinic acid with dry gaseous hydrogen chloride in xylene solution, the corresponding phosphorus trichloride and ethyldichlorophosphine were obtained. The method described was used to prepare perfluorovinylchlorophosphine. As a result of reacting per-

fluorovinylmagnesium iodide with the acid chloride of the tetraethyldiamide of phosphorous acid, the tetraethyldiamide of perfluorovinylphosphinic acid was obtained, and this was converted into trifluorovinyldichlorophosphine by the action of dry hydrogen chloride on its ethereal solution. The dichlorophosphine is a colorless liquid spontaneously inflammable in air.

In an analogous manner the diethylamide of bis-(trifluorovinyl)-phosphinic acid was obtained from $(C_2H_5)_2NP Cl_2$ and perfluorovinylmagnesium iodide, and it was then cleaved by dry hydrogen chloride to synthesize bis-(trifluorovinyl)-chloro-phosphine. Treatment of the latter with antimony trifluoride gave bis-(trifluorovinyl)-fluorophosphine as a colorless liquid, inflammable in air.

In distinction from the trifluoromethyl derivatives of arsenic and phosphorus, which are cleaved by the alkali in the cold with the separation of fluoroform [7], trifluoroethylene separates from tris-(trifluorovinyl)-arsine and tris-(trifluorovinyl)-phosphine only on heating; thus in the compounds described the perfluorovinyl radical does not possess pseudohalogen properties. On interaction of the compounds under discussion with aqueous alkali solutions water evidently adds across the double bond of the perfluorovinyl radical and hydrogen fluoride is lost from the layer; the number of fluoride ions found in the hydrolysate corresponds to six fluorine atoms.

EXPERIMENTAL

Reaction of perfluorovinyl iodide with phosphorus. Phosphorus (12 g) (washed with carbon disulfide and dried in vacuum in a stream of N_2) and perfluorovinyl iodide (18 g) were mixed in a stainless steel tube. The reaction mixture was heated at 180–200° for 40 hr, after which the tube was cooled to -70° and opened. The volatile products were trapped in a vessel cooled at -70°. They were fractionated in a stream of nitrogen to yield a fraction with b.p. 5–6° (3 g) and a fraction with b.p. 28–30° (10 g). The fraction boiling at 5–6° was perfluorocyclobutene, which was characterized as 1,2-dibromoperfluorocyclobutane, b.p. 95°; n_D^{20} 1.3902; d_4^{20} 2.1981. According to the literature

$\overline{CFBr-(CF_2)_2-CFBr}$ has b.p. 96°; n_D^{20} 1.3889; d_4^{20} 2.1974. The fraction with b.p. 30° was initial perfluorovinyl iodide; d_4^{20} 2.0764; n_D^{20} 1.3974.

Tris-(trifluorovinyl)-arsine. 5g arsenic trichloride was added at -18 to -15° over 40 min to perfluorovinylmagnesium iodide made from 21.2g $CF_2=CFI$ and 2.5g Mg in 80 ml ether. Then the reaction mixture was stirred at -20° for one hour, warmed to -10°, and decomposed with 17% hydrochloric acid (40ml). The ethereal layer was separated, and after drying over $MgSO_4$ was distilled in a stream of nitrogen. The following fractions were separated; a fraction with b.p. 56°/105–110mm (5.7g) which was discolored by iodine, and a fraction with b.p. 80–140°/105mm (1.5g). The first fraction was decolorized with metallic mercury and distilled a second time under nitrogen. A colorless liquid (3.6g, 40%) b.p. 58°/95mm, 50°/70mm, 110–111°/746mm was separated which was tris-(trifluorovinyl)-arsine; n_D^{18} 1.3998; d_4^{18} 1.8400. Found: F 54.1; As 23.20; C 22.42%; MR 41.2; mol.wt. 316.0, C_6F_9As . Calculated: F 53.77; As 23.57; C 22.46%; MR 41.07; mol. wt. 317.9.

Tris-(trifluorovinyl)-phosphine. Perfluorovinylmagnesium iodide was prepared from 16.0g $CF_2=CFI$ and 4.3g magnesium in 50ml absolute ether. To the ethereal solution of $CF_2=CFMgI$ at -20° was added 3.5g PCl_3 in 15ml ether. The reaction mixture became warm and an orange precipitate separated. After the addition of all the PCl_3 the reaction mixture was stirred for 1 hr, and then a condenser, a cold finger connected to two traps of -78° and 110°, and finally a Dreschel bottle containing sulphuric acid were connected to the flask. The system was flushed with nitrogen, and the ether evaporated. The residue was distilled in vacuum. The condensate which collected in the first trap (the second remained empty) was redistilled from a Favorskii flask in a stream of nitrogen. After removing the ether a fraction with b.p. 55–80° (0.3g) and a fraction with b.p. 98–102° (2.5g) were separated. The latter was decolorized with a drop of metallic mercury and redistilled a second time in a stream of nitrogen to give a colorless substance with b.p. 99–101°; $n_D^{23.5}$ 1.615, which was tris-(trifluorovinyl)-phosphine; yield 35.4%. Found F 63.76; P 10.92%; MR 39.39; mol. wt. 251.4, C_6F_9P . Calculated: F 62.4; P 11.32%; MR 39.20; mol. wt. 271.0.

Tris-(trifluorovinyl)-stibine. An ethereal solution of freshly distilled $SbCl_3$ (8.3g) was added with vigorous stirring to an ethereal solution of $CF_2=CFMgI$ (from 28.8g $CF_2=CFI$). The temperature of the reaction mass was maintained at -35 to -40°. After addition of all the $SbCl_3$ the mixture was stirred for 2 hr. Then the reaction mass was decom-

* The reactions of $CF_2=CFBr$ and $CF_2=CFCI$ with phosphorus, of $CF_2=CFCI$ with arsenic, and the dimerization of perfluorovinyl iodide were carried out under similar conditions.

posed with a saturated aqueous solution of NH_4Cl . The ethereal solution was washed with water, dried over MgSO_4 , and distilled. There was obtained 5.4g (41% yield) of a substance with b.p. 75-75.5°/74mm; n_D^{24} 1.1490, d_4^{24} 2.06. Found: F 46.5; Sb 34.0%; MR 44.76. $\text{C}_6\text{F}_9\text{Sb}$. Calculated: F 46.8; Sb 33.4%; MR 45.56.*

10-Trifluorovinyl-5,10-dihydrophenarsine. 51 g of adamsite was added in small portions from a retort to a solution of $\text{CF}_2=\text{CFMgI}$ (from 87g of $\text{CF}_2\text{:CFI}$ and 10.8g of magnesium) in 420 ml absolute ether at -20°. The mixture was stirred for one hour at -20° after the addition of the adamsite, and was left overnight. The next day the mixture was added to 400ml of 25% sulphuric acid at -15 to -10° with vigorous stirring. The ethereal solution was separated, the aqueous layer was extracted with ether, and the combined ether extracts were dried over calcined MgSO_4 . The ether was evaporated to leave a residue of a yellow crystalline substance (58g) [yield 75% m.p. 122° (from alcohol)] which was 10-trifluorovinyl-5,10-dihydrophenarsine. Found: As 23.13; F 18.45; N 4.30% . $\text{C}_{14}\text{H}_9\text{AsF}_3\text{N}$. Calculated: As 23.3; F 17.65; N 4.34%.

Trifluorovinyl-dichloroarsine. In a stainless steel tube of volume 70 ml was placed 12.4 g of $\text{CF}_2=\text{CFA}(\text{C}_6\text{H}_4)_2\text{NH}$ (dried over P_2O_5); the tube was cooled to -110°, and then 50 ml of liquid HCl was added. The tube was hermetically sealed and shaken for 1.5 hr. ** After evaporating the hydrogen chloride from the tube at room temperature, the tube was heated on a boiling water bath (at 12-15 mm) and a colorless liquid with a sharp irritating smell distilled and was collected in a tube (8.3 g). The residue in the tube was diphenylamine hydrochloride (7.8 g). The liquid products from the four traps were dried over MgSO_4 and distilled to give perfluorovinyl-dichloroarsine (28.0 g, 92.5%) with b.p. 115°; n_D^{20} 1.4820; d_4^{20} 1.9800. Found: C 10.58, As 32.6* *; Cl 30.92* *; Cl 31.75* *; F 25.30%* *; MR 32.59; mol. wt. 219.0. $\text{C}_2\text{F}_3\text{AsCl}_2$. Calculated C 10.57; As 33.0; $\text{Cl}_{\text{hydroly}}^*$: $\text{Cl}_{\text{fused}}^*$ 31.70; F 25.10%; MR 31.65****; mol. wt. M 227.0.

21 g of dry 10-perfluorovinyl-5,10-dihydrophenarsine was placed in a 150 ml flask equipped with a stirrer, an inlet tube for hydrogen chloride, and a straight condenser with a trap. A U-tube, with water in it to absorb HCl , was attached to the trap and subsequent to this a drying train (H_2SO_4 , CaCl_2) and two traps cooled to -110°. A stream of hydrogen chloride was passed through the molten substance for 4.5 hr, at first slowly, and then more rapidly. The bath temperature was maintained at 140-160° initially (30 min) and then at 180-210°.

At a bath temperature of 160° a gas began to condense in the trap. Most of the gas collected at 180-185°. The gas was trifluoroethylene, a total of 3.6 g (68%) b.p. -55° (according to the literature $\text{CF}_2=\text{CFH}$ boils at -56°). Found: molecular weight 80.95. Calculated for $\text{C}_2\text{F}_3\text{H}$; mol. wt. 82.0. By reacting the gas obtained with bromine (140°, 4 hr.) $\text{CF}_2\text{Br}=\text{CFHBr}$ was obtained, b.p. 76-77°, n_D^{26} 1.4105. Literature data for $\text{CF}_2\text{Br}=\text{CFHBr}$; b.p. 76.5° n_D^{14} 1.4145. At a bath temperature of 185-190° a yellowish liquid slowly began to distil (7.1 g). After a short time the bath temperature was raised to 225° and at this temperature distillation of the liquid ceased. As a result of a double fractionation at normal pressure a product, arsenic trichloride, was obtained, 3.6 g with b.p. 128°; $n_D^{21.5}$ 1.5935; $d_4^{21.5}$ 2.16. Found: As 41.4%. AsCl_3 . Calculated: As 41.3%. The residue in the flask consisted of a brownish mass (12 g) and a small quantity of sublimable white crystals, m.p. 174°, of diphenylamine hydrochloride. After treating the product mass with 15% NaOH and subsequently distilling the mixture, 8.7 g (79% yield) of diphenylamine was obtained; b.p. 138-139° / 5 mm, m.p. 48-49° (from ligroin). A mixed melting point with a pure sample of diphenylamine which melted at 50-51° gave no depressions.

Cleavage of $\text{CIP}[\text{N}(\text{C}_2\text{H}_5)_2]_2$ with hydrogen chloride. In a three necked flask fitted with a stirrer, a bubbler, and an outlet tube were mixed 19.6 g of $\text{CIP}[\text{N}(\text{C}_2\text{H}_5)_2]_2$ and 20 ml of absolute xylene. The outlet tube was connected to an ampoule, cooled to -70°, and a Dreschel bottle containing concentrated H_2SO_4 . The flask was submerged in a bath of ice water, and a stream of dry hydrogen chloride was passed into the stirred reaction mixture. An abundant white precipitate was formed, which completely dissolved on passing in further HCl . Two layers were formed. The lower layer was separated and distilled from a Favorskii flask. As a result, a fraction boiling at 80-130° (9.5 g) was separated; after a second distillation, 6.6 g (47.2% yield) of a substance with b.p. 74-76°; d_4^{20} 1.57, was obtained. According to the literature PCl_3 has b.p. 76°; d_4^{20} 1.57. Found: Cl 76.8% PCl_3 . Calculated: Cl 77.5%. The upper layer was heated on a water bath and after removal of the excess HCl , the whole reaction mass crystallized; weight of residue, 23.5 g; m.p. 214° (from ethanol-ether). According to the literature, diethylamide hydrochloride ($\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HCl}$ melts at 215-217°.

* AR_{Sb} 16.2

**The reaction can be carried out by mixing $\text{CF}_2=\text{CFA}(\text{C}_6\text{H}_4)_2\text{NH}$ and liquid HCl in a glass ampoule. The residue after evaporation of the HCl was a liquid which was distilled to give $\text{CF}_2\text{:CFA}(\text{C}_6\text{H}_4)_2\text{NH}$ in 25% yield.

**Arsenic was determined iodometrically; chlorine by the Volhard technique after hydrolysis.

***Fusion with metallic sodium.

**** Ar_{As} = 10.15.

The tetraethyldiamide of ethylphosphinic acid.* To an ethereal solution of C_2H_5MgBr (from 10.9 C_2H_5Br and 2.4 g magnesium) in a three-necked flask fitted with a stirrer, a dropping funnel and a reflux condenser, was added 18.1 g $CIP[N(C_2H_5)_2]_2$ at such a rate that the ether boiled easily. It was observed that a white solid precipitated. After stirring the reaction mixture for 2 hr the precipitate was filtered off (11.5 g), the ether evaporated, and the residue distilled in vacuum in a stream of nitrogen. 8.85 g of a substance with b.p. 78-79° (4 mm) was separated. The substance was dissolved in ether and washed with water. The ether layer was dried over calcined $MgSO_4$, and the ether evaporated. On redistilling the residue a colorless substance with a very unpleasant smell was obtained (8.45 g); yield 48.6%; b.p. 72-73° (3 mm); n_D^{20} 1.4680; d_4^{20} 0.885. Found: P 14.86; 14.90%; MR 64.97. $C_{10}H_{25}N_2P$. Calculated: P 15.2%; MR 64.48.

Ethylidichlorophosphine. 25 g of $C_2H_5P \cdot [N(C_2H_5)_2]_2$ in 25 ml ether was placed in a three-necked flask fitted with a stirrer, a bubbler, and a reflux condenser, and through this solution was passed a stream of dry HCl at such a rate that the ether boiled slightly (the HCl was passed for 5 hr). A precipitate formed and redissolved. The reaction mixture was diluted with ether, the precipitated diethylamine hydrochloride filtered off (26 g), the ether evaporated, and the residue distilled from a Favorskii flask in a stream of nitrogen. 8.6 g (42.8% yield) of a substance with b.p. 110-115°; d_4^{20} 1.221 was separated. According to the literature $C_2H_5PCl_2$ has b.p. 114-117°; d 1.2952.

The tetraethyldiamide of perfluorovinylphosphinic acid. An ethereal solution of $CF_2 = CFMgI$ (obtained from 47 g $CF_2 = CFI$ and 6 g magnesium) was placed in a four-necked flask fitted with a thermometer, a stirrer, a dropping funnel, and an outlet tube connected to a Dreschel bottle filled with H_2SO_4 . The flask was cooled to -30° and the air from the reaction flask displaced by nitrogen. An ethereal solution of 39 g $CIP[N(C_2H_5)_2]_2$ was added to the vigorously stirred reaction mixture; the temperature of the reaction mass rose by 5-7°. When the first portion of $CIP[N(C_2H_5)_2]_2$ was added but after this the temperature rise became less noticeable. After all the $CIP[N(C_2H_5)_2]_2$ had been added the reaction mixture was stirred at -30° for two hr and then warmed to room temperature. A dark resinous precipitate appeared on the sides of the flask. The ether layer was decanted, the ether evaporated, and the residue distilled in vacuum in a stream of nitrogen. As a result fractions were obtained with b.p. 44-50° (24 mm); 2.45 g; and b.p. 75-77° (5 mm); 32.5 g. After a second distillation of the second fraction a colorless unpleasant substance (31.5 g, 53.6% yield) was separated with b.p. 89-90° (11 mm); n_D^{20} 1.4470; d_4^{20} 1.054. Found: P 12.27; F 22.9; N 10.68%; MR 64.89. $C_{10}H_{20}N_2PF_3$. Calculated: P 12.1; F 22.12; N 10.94%; MR 64.01.

The diethylamide of bis-(trifluorovinyl)-phosphinic acid. The reaction between $CF_2 = CFMgI$ (from 45 g $CF_2 = CFI$) and $Cl_2PN(C_2H_5)_2$ (16.5 g) was carried out in an analogous way to the previous example. After evaporating the ether the residue was distilled in a stream of nitrogen to yield a fraction with b.p. 49-53° (18 mm) 10.2 g. ** After a second distillation of this fraction 9.4 g of a colorless unpleasant substance was obtained. Yield 37.5% with b.p. 60° (25 mm); n_D^{20} 1.4098; d_4^{25} 1.291. Found: P 11.23; F 43.76%; MR 50.86. $C_8H_{10}PNF_6$. Calculated: P 11.69; F 43.00%; MR 51.35.

Perfluorovinylidichlorophosphine. 19.9 g $CF_2 = CFP[N(C_2H_5)_2]_2$ in 50 ml absolute ether was placed in a three-necked flask fitted with a stirrer, a bubbler, and an outlet tube connected to a Dreschel bottle containing concentrated H_2SO_4 . The flask was placed in an ice water bath, and a stream of dry HCl passed through the vigorously stirred reaction mixture until the theoretical increase in weight (11.35 g) was obtained. The precipitated diethylamine hydrochloride (16.7 g) was filtered off under nitrogen. After evaporating off the ether, the residue was distilled up a column from a Favorskii flask in a stream of nitrogen to give a fraction (9.4 g) boiling at 83-85°, a fraction (0.7 g) boiling at 85-105°, and a residue (1.5 g). After distilling the first fraction a second time a colorless substance with a sharp smell was separated (9.42 g, 66% yield). The substance fumes in air with b.p. 81.5-82°; n_D^{19} 1.4412; d_4^{19} 1.574. Found: hydrolyzable Cl 38.80; F 31.5; P 16.90%; mol. wt. 186.7; MR 30.71. $C_2F_3PCl_2$. Calculated: hydrolyzable Cl 38.80; F 31.18; P 16.92%; mol. wt. 183.0; MR 30.02.

Bis-(trifluorovinyl)-chlorophosphine. By a similar method bis-(trifluorovinyl)-chlorophosphine (6.2 g, 60% yield) was obtained from 12 g of the diethylamide of bis-(trifluorovinyl)-phosphinic acid in 60 ml diethyl ether. It is a colorless substance with a sharp smell which fumes in air with b.p. 94-95°; n_D^{23} 1.4095; d_4^{23} 1.550. Found: P 13.63; F 49.47; Cl 15.42%; MR 36.29; mol. wt. 215.2. C_4F_6PCl . Calculated: P 13.55; F 49.98; Cl 15.51%; mol. wt. 228.5; MR 34.98.

* This work was carried out with the help of E. P. Shcherbina and L. F. Razgovorov.

** It is impossible to distill the substance completely because the residue decomposes explosively.

Perfluorovinylidifluorophosphine. 27.5 g freshly heated SbF_3 was placed in a 25 ml two-necked flask fitted with a dropping funnel and cold finger cooled with ice water. The cold finger was connected to two ampoules cooled at -78° , in the first of which was placed a little SbF_3 . The second ampoule was connected to a Dreschel bottle containing concentrated H_2SO_4 . The system was flushed with dry, oxygen-free nitrogen, and 8.0 g perfluorovinylidichlorophosphine was added from the dropping funnel. The flask was heated on a water bath at $50-60^\circ$; the product which distilled was collected in the ampoule containing SbF_3 . The distillate was warmed to 0° , held at this temperature for 30 min and then distilled into the second ampoule (4.2 g, 64% yield). The substance was a colorless liquid, spontaneously inflammable in air, b.p. $2-3^\circ$. Found %: F 63.69; P 20.80%. $\text{C}_2\text{F}_5\text{P}$. Calculated: F 65.33; P 20.66%.

Bis-(trifluorovinyl)-fluorophosphine. 4.5 g of dry SbF_3 were placed in a 25 ml reaction flask fitted with a dropping funnel and a condenser. A cold finger was attached to the condenser, and then two traps at -78° , and finally a Dreschel bottle filled with conc. H_2SO_4 . The system was flushed with dry oxygen-free nitrogen, and the cold finger filled with ice water. 3.2 g $(\text{CF}_2 = \text{CF})_2\text{PCl}$ were introduced into the flask through the dropping funnel, and the reaction mixture was heated on the water bath for 30 min. Water was removed from the cold finger and the reaction mixture was distilled to give a colorless substance (yield 50%) with b.p. $63-65^\circ$, which inflamed in air. Found: P 14.38; F 62.67%. $\text{C}_4\text{F}_7\text{P}$. Calculated: P 14.62; F 62.9%.

SUMMARY

1. As a result of the reaction between perfluorovinylmagnesium iodide and PCl_3 , AsCl_3 , and SbCl_3 , the corresponding tris-(trifluorovinyl)-phosphine, tris-(trifluorovinyl)-arsine, and tris-(trifluorovinyl)-stibine were obtained.
2. Amides of the type $\text{CIP}(\text{NR}_2)_2$ reacted smoothly with $\text{R}'\text{MgX}$ (where R' is alkyl or perfluoroalkenyl) to form substituted amides of the alkyl or perfluoroalkenyl phosphinic acids.
3. Cleavage of amides of the type $\text{R}'\text{P}(\text{NR}_2)_2$ with dry hydrogen chloride led to the formation of primary and secondary chlorophosphines; in this way $(\text{C}_2\text{H}_5)_2\text{PCl}_2$, $\text{CF}_2 = \text{CFPCl}_2$, $(\text{CF}_2 = \text{CF})_2\text{PCl}$ were obtained. By exchange of chlorine with fluorine in the last two substances we obtained $\text{CF}_2 = \text{CFFF}_2$ and $(\text{CF}_2 = \text{CF})_2\text{PF}$.
4. The reaction of perfluorovinylmagnesium iodide with 10-chloro-5, 10-dihydrophenarsine gave 10-perfluorovinyl-5,10-dihydrophenarsine, which was converted into perfluorovinylidichloroarsine in the quantitative yield by liquid hydrogen chloride.

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RELATIVE REACTIVITY OF ω -TRIALKYSILYL
SUBSTITUTED ALCOHOLS AND MERCAPTANS
WITH PHENYLISOCYANATES.

V. F. Mironov and N. A. Pogonkina

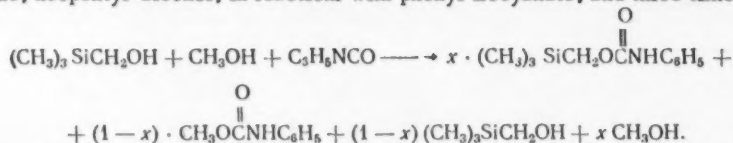
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 11,

pp. 1998-2002, November, 1960

Original article submitted May 29, 1959

Davies and Farnum [1] developed a method for determining the relative reactivities of aliphatic alcohols. The method consists of carrying out a reaction between a mixture of two equivalents of the alcohols (one equivalent of each) with one equivalent of phenyl isocyanate. From the molar ratio of the two phenylurethanes formed are calculated the relative reaction rates constants of the two alcohols being compared. Sprier, Daubert, and McGregor [2] used this method to estimate the relative reactivity of trimethylsilylmethanol, which appeared to be six times as reactive as its carbon analogue, neopentyl-alcohol, in reactions with phenyl isocyanate, and three times as active as methanol:



In this paper we have in the same way estimated the reactivity of organosilicon alcohols and mercaptans of the following homologous series: $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OH}$ and $(\text{C}_2\text{H}_5)_2\text{CH}_3\text{Si}(\text{CH}_2)_n\text{SH}$ where $n=1, 2$, and 3 . To this end, one equivalent of phenyl isocyanate was added to a mixture of equivalent quantities of the organosilicon alcohol being studied and methanol. The solvent and the unreacted molecules were distilled from the mixture. Analysis for the percentage silicon content of the mixed urethanes permitted us to calculate the molar quantity of the organosilicon alcohol used up in the reaction by means of the following formula:

$$X = \frac{M^C \cdot p}{M^{\text{Si}} \cdot p + p \cdot M^C - pM^{\text{Si}}},$$

where M^C is the molecular weight of the organic urethane; M^{Si} is the molecular weight of the organosilicon urethane; p the silicon content of the organosilicon urethane in %; X is the silicon content found in the mixture of the two urethanes in %; x is the molar content of the organosilicon urethane in the mixed urethanes.

The relative reaction rate constants of the two alcohols being compared is calculated from the formula:

$$\frac{K^{\text{Si}}}{K^C} = \frac{\lg(1-x)}{\lg x},$$

where K^{Si} and K^C are the reaction rate constants for the organosilicon alcohols and methanol. The results obtained for three organosilicon alcohols are cited in Table 1.

TABLE 1

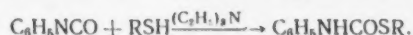
Organosilicon alcohol	Si, %	K^{Si}/K^C
$(\text{CH}_3)_3\text{SiCH}_2\text{OH}$	9,25	2,5
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{OH}$	7,60	1,14
$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$	7,20	1,13

TABLE 2

Organosilicon mercaptan	Si, %	K^{Si}/K^C
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiCH}_2\text{SH}$	4,50	0,46
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiCH}_2\text{CH}_2\text{SH}$	7,90	4,57
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SH}$	7,50	4,85

From Table 1 it follows that the trimethylsilylmethanol is 2.5 times as active as methanol (close to that determined by Sprier [2] - 2.9 times), about twice as active as both neighbouring homologs: β -trimethylsilyethanol and α -trimethylsilylpropanol.

It is known [3] that mercaptans also react with phenyl isocyanate in the presence of traces of triethylamine:



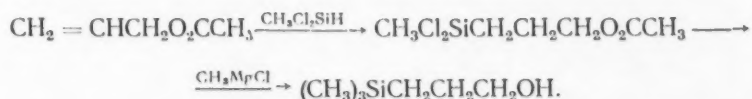
In this connection we estimated the relative reactivity of organosilicon mercaptans of the homologous series $(\text{C}_2\text{H}_5)_2\text{CH}_3\text{Si}(\text{CH}_2)_n\text{SH}$ by comparison with butylmercaptan, using the same techniques and calculations as in the case of the organosilicon alcohols. The results are cited in Table 2.

Diethylmethylsilylmethyl mercaptan was shown to be approximately half as reactive as butyl mercaptan, and about one tenth as reactive as its closest homologs with substituents β - and γ - to the thiol group. Thus in both the ω -trialkylsilyl alcohols and the ω -trialkylsilyl mercaptans the change in reactivity on moving the functional group from the silicon changes sharply on moving the γ - and β -position, and is almost unchanged on its further movement to the γ -position. The expected anomaly in reactivity for compounds with thiol and hydroxyl groups in the β -position was not detected by us.

the results obtained by us can be explained by the rapid fading of the positional inductive effect of the electron-donating trialkylsilyl group, which is naturally strongest in compounds with the functional group in the α -position. However, the presence of conjugation between the Si-C bond and the unshared pair of the oxygen and sulphur in the compounds $\text{R}_3\text{Si}-\text{CH}_2\text{OH}$ and $\text{R}_3\text{Si}-\text{CH}_2\text{SH}$ is not excluded. This shows in the marked difference of reactivity of these compounds from both neighboring homologs with functional groups further away from the silicon.

Analysis of the combination diffusion spectra of the organosilicon alcohols and mercaptans under investigation also allows one to note the exceptional nature of compounds with active groups in the α -position. The frequency of the valence vibration $\nu_{\text{Si}-\text{C}}$ in α -silicon alcohols (592 cm^{-1}) and α -silicon mercaptans (556 cm^{-1}) is decreased in comparison with the frequency in compounds with functional groups in the β - and γ -position relative to the silicon atom (for alcohols 612 and 607 cm^{-1} , for mercaptans 579 and 578 cm^{-1} , respectively). In the Raman spectra of silicon alcohols we did not observe bands corresponding to OH vibrations because of their low intensities. We therefore turned to the IR-spectra in which we found broad bands in the region $3300\text{--}3500\text{ cm}^{-1}$, corresponding to the vibration of hydrogen bonded groups.

The initial silicon mercaptans were synthesized by a method developed by us earlier [4]. γ -Trimethylsilylpropanol was made by a new route:



The high yield and purity of the product obtained cause this method to be considered to be better than that described earlier in the literature [5]. Attempts to obtain γ -diethylmethylsilylpropanol by the addition of $(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiH}$ to allyl alcohol in the presence of hexachloroplatinic acid led only to the formation of allyloxytrimethylsilane.

EXPERIMENTAL

γ -Trimethylsilylpropanol, $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OH}$. $\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OCOCH}_3$ (180g) [6] was added to CH_3MgCl obtained from 100 g magnesium in 1.5 liters absolute ether. The contents of the flask were boiled for 5 hr and decomposed with 5% hydrochloric acid. The ethereal layer was separated from the aqueous layer; the latter was extracted with ether and the combined ether extracts dried over Na_2SO_4 . The ether was evaporated and the residue distilled in vacuum to yield 87 g γ -trimethylsilylpropanol b.p. 73.5° (15mm); n_D^{20} 1.4270; yield 79%. Literature data [5]: b.p. 83° (27mm); n_D^{20} 1.4290.

Raman Spectrum*

$\Delta\nu$, cm^{-1} : 147 (2 sh); 205 (5 v. br); 251 (1); 325 (2); 582 (2); 609 (10); 694 (4 br); 752 (0); 1018 (2); 1138 (1 v. br); 1189 (2 v. br); 1249 (1 br); 1298 (1 br); 1409 (4 br); 1452 (1 sh); 2895 (10 v. br); 2951 (10 br).

*The Raman spectra were obtained in an ISP-51 apparatus with a central chamber. The intensities are reduced to a ten-point visual scale. (sh = sharp; br. = broad)

β -Trimethylsilylethanol $(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{OH}$ was synthesized as described in [6] by reacting CH_3MgCl and $\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{OCOCCH}_3$ in the conditions of the previous experiment.

Raman Spectrum

$\Delta\nu$, cm^{-1} : 149 (2); 207 (5 br); 240 (3 br); 305 (0); 385 (2 br); 580 (6 sh); 612 (10 sh); 663 (0); 694 (5 br); 761 (0); 837 (1.5); 939 (1 br); 1001 (22); 1041 (1 br); 1130 (1 v. br); 1186 (2 br); 1252 (1 br); 1296 (1 br); 1413 (4 br); 1474 (0 br); 2893 (10); 2952 (10).

β -(β -Trimethylsilylethoxy)-propionitrile $(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CN}$. To 11.8 g (0.1 M) of β -trimethylsilylethanol were added two drops of a syrup of sodium methoxide in methanol and then 8 g (0.15 M) of acrylonitrile. The contents of the flask were warmed. After 24 hr the mixture was washed with acidified water, dried and broken up. 14 g of β -(β -trimethylsilylethoxy)-propionitrile was obtained with b.p. 130-133° (15 mm), n_D^{20} 0.8861; d_4^{20} 1.4350; 81.7% yield.

Found: C 56.38, 56.40; H 9.95, 10.12; Si 16.10, 16.10%; MR 50.44. $\text{C}_8\text{H}_{17}\text{SiON}$. Calculated: C 56.08; H 10.00; Si 16.39%; MR 50.45.

Raman Spectrum

$\Delta\nu$, cm^{-1} : 145 (2); 201 (5 v. br); 215 (1 br); 240 (5 br); 592 (10); 670 (2 br); 698 (4 br); 845 (1 br); 860 (1 br); 1008 (1 br); 1138 (0); 1201 (0 br); 1249 (1 br); 1322 (0); 1415 (3 br); 2894 (10); 2955 (10).

β -(Methyldiethylsilyl)-ethylthioacetate $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}_2\text{CH}_2\text{SCCH}_3$. To 28.7 g (0.22 M) $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}=\text{CH}_2$ was added 21 ml (0.3 M) thioacetic acid. The mixture was boiled for 6 hr. By vacuum distillation 25.2 g β -(methyldiethylsilyl)ethylthioacetate was separated, b.p. 122° (19 mm); n_D^{20} 1.4752; d_4^{20} 0.9345; found: MR 61.60; calculated: MR 61.75; yield 55.1%.

γ -(Methyldiethylsilyl)-propyl thioacetate $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{SCCH}_3$ was prepared in a similar way from $\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiCH}_2\text{CH}=\text{CH}_2$ and thioacetic acid; b.p. 143° (26 mm); n_D^{20} 1.4749; d_4^{20} 0.9277; found: MR 66.26; calculated: MR 66.38; yield 63%.

γ -Thiolpropyldiethylmethylsilane, [γ -(diethylmethylsilyl)-propanethiol], $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{CH}_3$. 39.6 g (0.18 M) $(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SCOCCH}_3$ was added to a solution of 7.4 g NaOH in 37 ml water and 15 ml ethanol. The mixture was boiled with vigorous stirring in a nitrogen atmosphere for 17 hr. The organic layer was separated, dried over Na_2SO_4 and distilled. 23.7 g γ -thiolpropyldiethylmethylsilane was obtained with b.p. 100° (18 mm); n_D^{20} 1.4684; d_4^{20} 0.8718; found: MR 56.27; calculated: MR 56.35; yield 74%.

Raman Spectrum

$\Delta\nu$, cm^{-1} : 149 (3 sh); 248 (2 v. br); 313 (0 br); 473 (0); 516 (1); 559 (1); 578 (10); 659 (5 br); 697 (0); 754 (3 br); 778 (0); 809 (1 br); 860 (0 br); 916 (1 br); 975 (3 br); 1016 (4 br); 1114 (2 br); 1174 (1 br); 1233 (3); 1256 (2 br); 1300 (1); 1379 (1); 1415 (6); 1462 (6); 2576 (3); 2880 (10); 2901 (10); 2930 (1); 2963 (10).

β -Thioethyldiethylmethylsilane, [β -(diethylmethylsilyl)-ethanethiol], $\text{HSCH}_2\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{CH}_3$ was obtained in a similar way from $(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiCH}_2\text{CH}_2\text{SCCH}_3$. 14.2 g β -thioethyldiethylmethylsilane (72.0% yield) was obtained with b.p. 82° (15 mm); n_D^{20} 1.4690; d_4^{20} 0.8751; found: MR 51.78; calculated: MR 51.57; yield 72.0%.

Raman Spectrum

$\Delta\nu$, cm^{-1} : 148 (3 sh); 230 (1 v. br); 251 (3 v. br); 305 (1 br); 373 (0 br); 557 (3 br); 579 (10); 654 (1 br); 690 (4 v. br); 717 (3 v. br); 757 (3); 815 (3 br); 875 (10); 930 (0); 977 (3); 1016 (5 v. br); 1122 (2 br); 1177 (3 br); 1237 (3 br); 1280 (4 br); 1381 (1); 1415 (6); 1463 (6); 2575 (4); 2884 (10a); 2933 (1); 2959 (9 sh).

α -Thiolmethyldiethylmethylsilane, [α -(diethylmethylsilyl)-methanethiol], $\text{HSCH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{CH}_3$ was obtained by a method described earlier [7].

$\Delta\nu$, cm^{-1} : 148 (2 sh); 215 (0 br); 261 (1 br); 303 (1 br); 556 (10); 568 (5); 627 (0); 680 (0); 739 (4 br); 761 (3 br); 802 (2 br); 815 (1 br); 907 (2 br); 977 (4); 1018 (4 br); 1060 (1 br); 1118 (3 br); 1147 (1 br); 1191 (0); 1260 (4 v. br); 1302 (3 br); 1383 (1); 1415 (4); 1464 (6); 2577 (3); 2636 (3); 2885 (10); 2953 (10).

Reaction of phenyl isocyanate with mixtures of methanol and $(\text{CH}_3)_2\text{Si}(\text{CH}_2)_n\text{OH}$, where $n = 1, 2$, and 3 . An aliquot (equal to 0.05 M) of each organosilicon alcohol was added to 0.05 M of absolute methanol and 2 ml dry benzene. To each of the three mixtures obtained was added 0.05 M phenyl isocyanate dissolved in benzene. The mixture was allowed to stand for two days and then the solvent and the unreacted alcohols were evaporated at a pressure of ~ 2 mm. The residue was then heated under vacuum on a water bath at $70-80^\circ$ for 5 hr. The residue (crystalline in the case of α -silicon alcohols, oily in the case of β - and γ -silicon alcohols) was purified by dissolving it in petroleum ether, filtering, and removing the petroleum ether in vacuum to constant weight of the residue. The residue was analyzed for silicon by the method [8]. Six combustions were carried out for each alcohol, and the average value taken.

Reaction of phenyl isocyanate with mixtures of butyl mercaptan and $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_2)_n\text{SH}$, where $n = 1, 2$, and 3 . Mixtures of butyl mercaptan, silicon mercaptan and phenyl isocyanate were made up in the same way as for the organosilicon alcohols. A drop of triethylamine was added to each mixture. After standing for 10 days at room temperature, the solvents and unreacted mercaptans were removed, and the percentage of silicon in the residues was determined.

The Raman spectra were taken and interpreted by L. A. Leites, to whom we extend one sincere thanks.

SUMMARY

1. In the homologous series of organosilicon alcohols of the type $(\text{CH}_3)_2\text{Si}(\text{CH}_2)_n\text{OH}$, the relative reactivity towards phenyl isocyanate is in the following ratio $2.5 : 1 : 1$ for $n = 1 : 2 : 3$.

2. In the analogous series of mercaptans $(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Si}(\text{CH}_2)_n\text{SH}$ the reactivity towards phenyl isocyanate has the order $1 : 10 : 10$.

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A STUDY IN THE FIELD OF THE STEREOCHEMISTRY
OF CYCLIC COMPOUNDS

COMMUNICATION 35. SYNTHESIS AND CONFIGURATION OF THE ISOMERS
OF 7-METHOXY-1,2,3,4,4a,9,10,10a-OCTAHYDROPHENANTHRENE-1,
2-DICARBOXYLIC ACID WITH A CIS-CONNECTION OF CYCLES

V. F. Kucherov, L. K. Lysanchuk, and V. M. Andreev

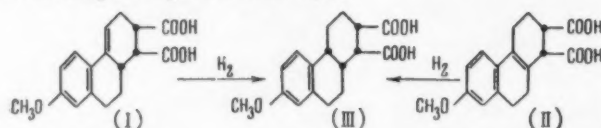
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No.11,

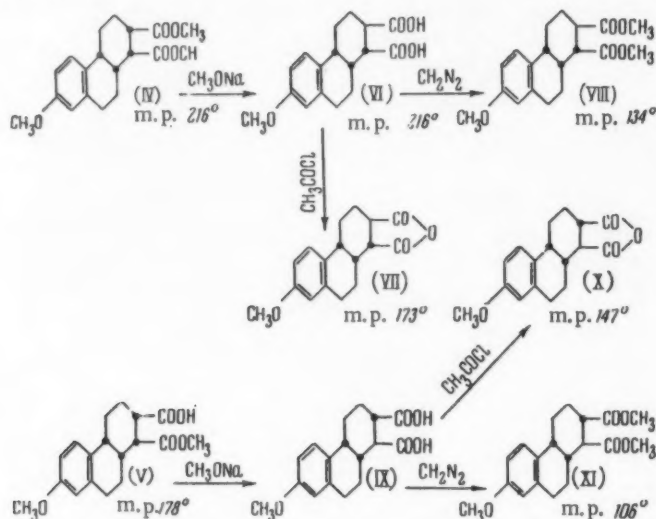
pp. 2003-2008, November, 1960

Original article submitted May 13, 1959

In one of our previous communications [1] we have shown that the catalytic hydrogenation of the tricyclic acids (I) and (II), which are isomeric with a different position of the double bond, leads to the cis-syn-cis acid (III), whose configuration has been established on the basis of the general rule of cis-addition of hydrogen on the side opposite to the carboxyl groups, this rule having been proven earlier [2].



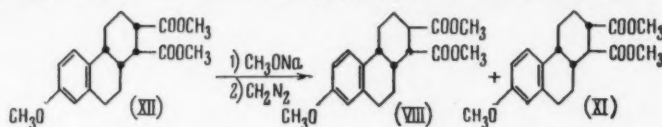
In order to solve the problem of the configuration of this acid in an unequivocal way, it was necessary to carry out the stereospecific synthesis of its other possible geometric isomers having a cis-connection of cycles. For this purpose, we used the isomeric half-esters (IV) and (V) which have been described earlier [3], and whose structure has been established on firm grounds.



It appeared that in distinction from the isomeric unsaturated half-esters which were studied before the two saturated half-esters (IV) and (V) are able to isomerize with change of configuration of the carbomethoxyl groups when boiled with sodium methoxide, different isomeric trans-acids being formed after subsequent hydrolysis. Under these con-

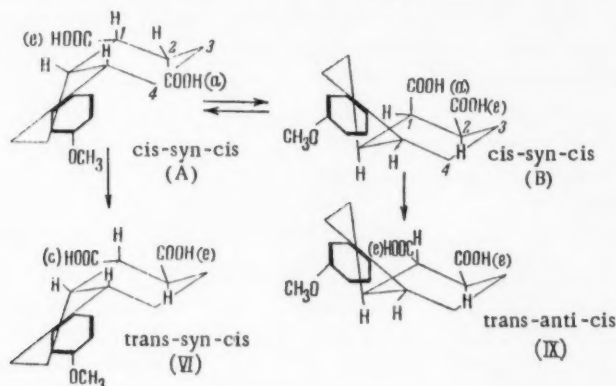
ditions, the *cis-syn-cis*-half-ester (IV) gives a good yield of *trans-syn-cis*-acid (VI), which has been characterized as its anhydride (VII) and diester (VIII). In an analogous way, the *cis-syn-cis*-half-ester (V) is isomerized to the *trans-anti-cis*-acid (IX), whose anhydride (X) and diester (XI) have also been prepared.

On the basis of the fact that in the *cis-syn-cis*-acid (III) one of the carboxyl groups must be axial, and the other equatorial, and that, at the same time, both of its half-esters (IV) and (V) are able to undergo isomerization, one can conclude that this acid must be prone to an easy ring conversion. If this is really so, then heating of its diester (XII) with sodium methoxide must lead to a mixture of the above mentioned isomeric *trans*-acids (VI) and (IX), as a result of a change of configuration of the carbomethoxyl group at C₁, as well as at C₂.



It was shown by specially designed experiments that, in fact, the *cis-syn-cis*-diester (XII), under the action of sodium methoxide, gives a mixture of isomeric acids from which, after treatment with diazomethane, it was possible to isolate (in the ratio 1:3) the *trans-syn-cis*- and the *trans-anti-cis*-diesters (VIII) and (IX).

A consideration of the molecular models shows that the *cis-syn-cis*-acid (III) can be represented as two possible interconvertible forms (A) and (B) each of which is sufficiently probable.



As one can judge from these models, an isomerization of the form (A) at the carboxyl group on C₂ would lead to the trans-syn-cis-acid (VI), whereas an isomerization of the form (B) at the carboxyl on C₁ would give the isomeric trans-anti-cis-acid (IX). In the case of the cis-syn-cis-diester (XII), both ways for isomerization are possible because of the availability of the conversion transformation, and this leads to a mixture of both the trans-acids.

However, all the reactions described above, which allowed us to prepare two new isomers of 7-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1,2-dicarboxylic acid, do not constitute final proof of the *cis-syn-cis*-configuration of the starting acid (III). Its configuration, and thus the configuration of all the other isomers can be considered to be definitely proved only if it were possible to carry out the stereospecific synthesis of the fourth possible isomer having a *cis-anti-cis*-configuration. As we have shown earlier [4-6], such a configuration in the case of isomers having a *cis*-connection of cycles is the most stable configuration, to which must be convertible by thermal isomerization all the other isomers of this type. This method for the synthesis of a geometric isomer with a definite configuration is sufficiently stereospecific, and it was used by us for the preparation of the required *cis-anti-cis* acid.

It appeared that all the isomeric anhydrides previously prepared (VII), (XI), and (XIII) are converted with good yields by thermal isomerization to the new anhydride (XIV) which must have, in conformity with such a method of formation, a *cis-anti-cis*-configuration. This conversion is effected more smoothly by boiling the isomeric anhydrides or the corresponding free acids in acetic anhydride solution. Hydrolysis of *cis-anti-cis*-anhydride (XIV) with 5% sodium hydroxide gave the corresponding *cis-anti-cis*-acid (XV), the ester of which (XVI) proved to be different from all the esters which were formerly described.



lization and melting at 118-128°. The crystalline hydrate was dried at room temperature in vacuum prior to analysis. Found: C 63.75, 63.64; H 6.64, 6.80%. $C_{17}H_{20}O_5 \cdot H_2O$. Calculated: C 63.34; H 6.89%.

When crystallized from benzene, the trans-anti-cis-acid forms a molecular compound with one molecule of benzene, m.p. 120-125°. Found: C 71.99, 71.92; H 6.95, 7.02%. $C_{17}H_{20}O_5 \cdot C_6H_6$. Calculated: C 72.25; H 6.86%.

For the preparation of the trans-anti-cis-anhydride (X), a mixture of 0.4 g of the crystalline hydrate of the acid (IX) in 20 ml of acetyl chloride was boiled for 5 hr. Vacuum distillation of the solution gave an oil which was treated with a mixture of ether and petroleum ether; the crystals thus obtained were filtered off and washed with ether. When a solution of this product in cold benzene was treated with ether, 0.25 g of pure trans-anti-cis-anhydride (X), m.p. 145-146°, separated out. Found: C 71.57, 71.37; H 6.31, 6.23%; $C_{17}H_{18}O_4$. Calculated: C 71.31; H 6.34%.

Hydrolysis of the trans-anti-cis-anhydride (X) with a 2% sodium hydroxide solution led to the initial crystalline hydrate of the trans-anti-cis-acid (IX).

Treatment of 0.2 g of the crystalline hydrate of the trans-anti-cis-acid (IX) with an ethereal solution of diazomethane gave a quantitative yield of the trans-anti-cis-diester (XI), which had a constant m.p. of 105-106° after two recrystallizations from ether. Found: C 68.38, 68.24; H 7.27, 7.31%. $C_{19}H_{24}O_5$. Calculated: C 68.65; H 7.28.

Isomerization of the cis-syn-cis-diester (XII) with sodium methoxide. A mixture of 0.56 g of the cis-syn-cis-diester (XII) and 25 ml of a 10% solution of sodium methoxide was boiled for 20 hr; the methanol was evaporated in vacuum, the residue dissolved in 40 ml of water and evaporated on a water bath to effect its hydrolysis. The precipitated salts were filtered, washed with methanol, dissolved in 30 ml of water, and acidified with dilute hydrochloric acid. The oil which separated out gradually set to a crystalline mass giving 0.38 g of a substance melting over a large temperature range (118-125°). The mixture of acids was treated with an ethereal solution of diazomethane. After evaporation of the solvents, the residual oil was treated with petroleum ether. A crystalline product (0.24 g), m.p. 90-100° was thus obtained. After slow recrystallization from ether with the subsequent mechanical separation of the crystals which separated out, 50 mg of the trans-syn-cis-diester (VIII), m.p. 130-132°, and 150 mg of the trans-anti-cis-diester (IX), m.p. 105-106°, were obtained. These substances did not give a melting point depression with the samples described above.

Thermal isomerization of the anhydrides (VII), (X), and (XIII). One fifth of a gram of the trans-syn-cis-anhydride (VII) was heated for 4 hr at 200-210° in a current of nitrogen, and the crystallized melt was washed on the filter with ether to give 0.16 g of a substance m.p. 196-200°. After a double recrystallization from acetone, the purified cis-anti-cis-anhydride (XIV) melted at 205-206°. Found: C 71.10, 71.30; H 6.39, 6.27%. $C_{17}H_{18}O_4$. Calculated: C 71.31; H 6.34%.

A mixture of 50 g of the trans-syn-cis-anhydride (VII) and 2 ml of acetic anhydride was boiled for 3 hr, and then evaporated in vacuum to incipient crystallization. The crystals were washed on the filter with ether; they gave 30 mg of a substance, m.p. 199-203°, which was purified by recrystallization from acetone yielding the pure cis-anti-cis-anhydride (XIV) melting at 203-205°, and identical with the substance described above.

A mixture of 0.30 g of the trans-syn-cis-acid (VI) and 20 ml of acetic anhydride was boiled for 5 hr; the warm solution was filtered and evaporated in vacuum to incipient crystallization. The cis-anti-cis-anhydride (XIV) (0.21 g) thus obtained had m.p. 205-206° after recrystallization from acetone (no depression with the sample prepared as described above.)

Boiling of a mixture of 50 mg of the trans-anti-cis-acid (IX) with 2 ml of acetic anhydride for 5 hr gave, after subsequent recrystallization of the product obtained from acetone, 27 mg of the cis-anti-cis-anhydride (XIV), m.p. 205-206°.

Boiling of a mixture of 70 mg of the cis-syn-cis-acid (III) with 3 ml of acetic anhydride for 5 hr led to a quantitative yield of the cis-anti-cis-anhydride (XIV).

Cis-anti-cis-acid (XV) and its diester (XVI). A mixture of 0.16 g of the cis-anti-cis anhydride (XIV) and 4 ml of a 5% solution of sodium hydroxide was heated to complete solution of the anhydride; the solution was diluted with an equal volume of water, filtered and acidified. The precipitate which separated out was filtered off, and washed with water giving 0.13 g of the cis-anti-cis acid (XV), m.p. 235-237°, which melted at 237-238° after drying in vacuum at 100°. Found: C 66.88, 66.93, H 6.52, 6.49%. $C_{17}H_{20}O_5$. Calculated: C 67.09; H 6.62%.

For the preparation of the diester, a suspension of 0.11 g of the cis-anti-cis-acid (XV) in 10 ml of methanol was treated with an ethereal solution of diazomethane. The oil remaining after removal of the solvents by distillation was treated with a mixture of ether and petroleum ether, 0.1 g of cis-anti-cis-diester, m.p. 83-85°, being obtained. After recrystallization from a mixture of ether and petroleum ether, the product melted at 85-87°. Found: C 68.78, 68.63; H 7.29, 7.31%. $C_{19}H_{24}O_5$. Calculated: C 68.65; H 7.28%.

Cis-anti-cis-half-ester (XVII) and its isomerization with sodium methoxide. A mixture of 0.50 g of the cis-anti-cis-anhydride (XIV) and 20 ml of absolute methanol was boiled for 4 hr. After removal of methanol in vacuum, the residue was washed on the filter with ether, giving 0.55 g of the cis-anti-cis-half ester (XVII), m.p. 164-169°, whose melting point rose to 171.5-172.5° after two recrystallizations from methanol. Found: C 68.11, 68.28; H 6.99, 6.96%. $C_{18}H_{22}O_5$. Calculated: C 67.90, H 6.97%.

To effect the isomerization, 0.34 g of the half-ester (XVII) was boiled for 18 hr with 15 ml of a 10% solution of sodium methoxide. After working up the mixture in the usual way, 0.30 g of a substance melting over a wide m.p. range (110-115°) was obtained. Crystallization from benzene led to 0.04 g of the starting cis-anti-cis-acid (XV), m.p. 235-235.5°, and 0.18 g of a substance, m.p. 115-120°. The latter, upon treatment with an ethereal solution of diazomethane gave 0.13 g of the corresponding diester, m.p. 95-97°. After recrystallization from ether, the trans-anti-cis-diester (XVI) melted at 102-105°, and did not depress the melting point of the sample obtained as described above.

SUMMARY

1. The synthesis of the four possible geometric isomers of 7-methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1,2-dicarboxylic acid with a cis-connection of cycles has been achieved, and their configurations have been proved.
2. The possibility of conversion transformations of the cis-syn-cis-acid (III) has been established; this possibility explains the formation of two isomeric trans-acids (VI) and (V), and the cis-syn-cis-diester (XII).

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CHEMISTRY OF DIHYDRORESORCINOL

COMMUNICATION 6. A NEW METHOD FOR THE SYNTHESIS

OF PHENANTHRENE DERIVATIVES FROM DIHYDRORESORCINOL

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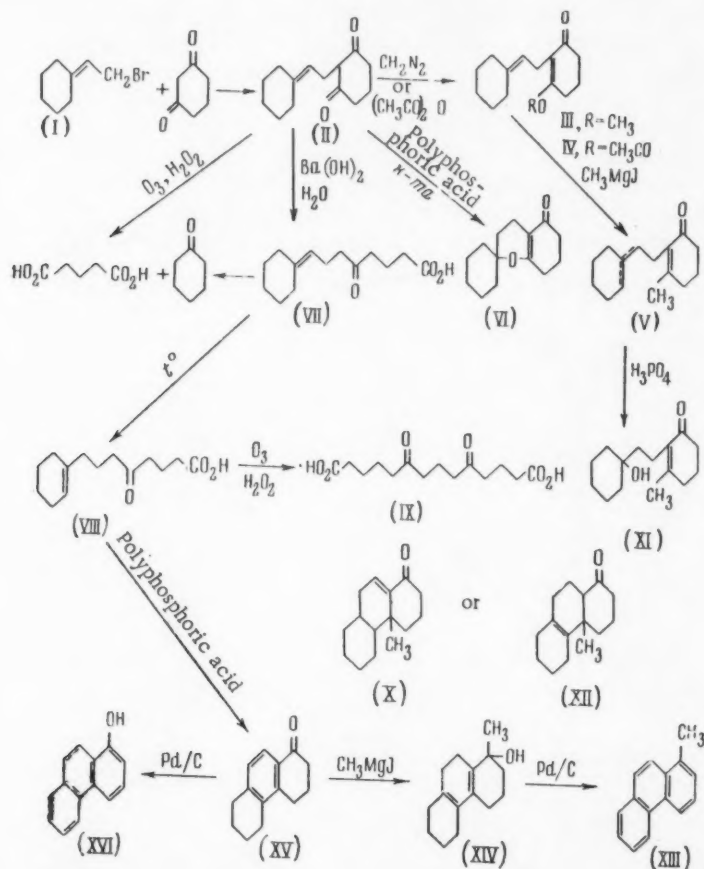
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In our previous communications [1,2], we described the preparation and the biological activity of the derivatives of 2-allyldihydroresorcinol. As a continuation of these researches, we undertook in the present work an attempt to use the above mentioned products for the synthesis of polycyclic compounds related to steroids.

As a starting material we took 2-(β -cyclohexylideneethyl) dihydroresorcinol (II), which is obtained with a yield of about 50% during the condensation of the Na-derivative of dihydroresorcinol with 1-bromo-2-cyclohexylideneethane (I). The position of the double bond in the molecule of 2-(β -cyclohexylideneethyl) dihydroresorcinol has been confirmed by ozonolysis, which led to cyclohexanone and glutaric acid,



It was not possible to cyclize the diketone itself to the corresponding phenanthrene derivative (XX), as ring closure of the stable oxygen-containing cycle occurred during heating of this substance with polyphosphoric acid.

An analogous reaction has been described earlier by Nazarov, Torgov, and Anachenko [3] who obtained 2,2-dimethyltetrahydrochroman-5-one (XVIII) by the action of phosphorus anhydride on 2-(α,α -dimethylallyl) dihydroresorcinol (XVII).

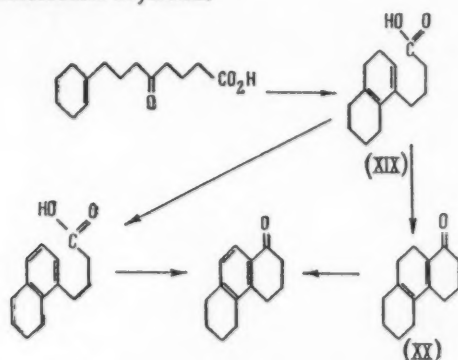


In the light of this information, we found it purposeful to investigate the byways by which polycyclic carbocyclic systems can be produced from derivatives of 2-allyldihydroresorcinol by making use of the intermediate compounds having no β -diketo groups.

By reaction of the enol ester of 2-(β -cyclohexylideneethyl) dihydroresorcinol (III) with methyl magnesium iodide with a subsequent hydrolysis of the product of the Grignard reaction, the bicyclic unsaturated ketone (V) has been obtained. It appears that the unsaturated ketone (V) probably does not contain a semi-cyclic double bond, as its ozonolysis did not lead to the isolation of cyclohexanone. All attempts to effect cyclization of the unsaturated ketone (V) to the tricyclic ketone (X) or (XII) did not lead to the expected results. Under the action of 80% phosphoric acid, the unsaturated ketone (V) gave, as a result of the hydration of the unconjugated double bond, the keto alcohol (XI), the structure of which has been confirmed by its ultraviolet spectrum.

Treatment of the unsaturated ketone (V) with polyphosphoric acid gave, together with tarry products, a small amount of the keto alcohol (XI). Hydrolysis of 2-(β -cyclohexylideneethyl) dihydroresorcinol (II) with barium hydroxide led to the formation of a mixture of the isomeric acids (VII) and (VIII), differing by the position of the double bond. As a result of ozonolysis of the crystalline keto acid (VII) containing a semi-cyclic double bond, cyclohexanone was obtained, whereas ozonolysis of the liquid keto acid (VIII) gave 4,8-diketododecane-1,12-dicarboxylic acid (IX). By vacuum distillation, the crystalline keto acid (VII) was isomerized to the liquid isomer (VIII). Under the influence of polyphosphoric acid, the unsaturated keto acid (VIII) underwent a double cyclization with the formation of 1-keto- $\Delta^{9,11,13}$ -octahydrophenanthrene (XV), the structure of which was proved by its ultraviolet spectrum and its dehydrogenation reactions. By full aromatization with the help of palladium-charcoal, the ketone (XV), and the alcohol derived from it (XIV) gave phenanthrene-1-ol (XVI) and 1-methylphenanthrene (XIII), respectively.

The above mentioned conversion of the unsaturated keto acid (VIII) to 1-keto- $\Delta^{9,11,13}$ -octahydrophenanthrene (XV) obviously takes place through several steps, including the formation of the diene acid (XIX) and the dienone (XX), as well as aromatization and intramolecular acylation.



This series of reactions provides great possibilities for the synthesis of miscellaneous polycyclic compounds related to steroids.

EXPERIMENTAL

Preparation of 2-(β -cyclohexylideneethyl) dihydroresorcinol (II). A solution of the sodium derivative of dihydroresorcinol prepared from 81 g of dihydroresorcinol, 600 ml of methanol and the equivalent amount of sodium was

treated during 30 min with stirring and cooling to -5° to -12° , with 137 g of 1-bromo-2-cyclohexylideneethane (I) [4] (b.p. $67-69^{\circ}$ at 3 mm). The temperature of the reaction mixture was slowly raised to room temperature; then the mixture was stirred for a further 2 hr while boiling. After removal of methanol by distillation, the residue was treated with a solution of 80 g of sodium carbonate in 400 ml of water. Acidification of the alkaline solution led to the separation of 83.4 g (52%) of 2-(β -cyclohexylideneethyl) dihydroresorcinol (II), m.p. $165-166^{\circ}$ (from aqueous methanol). Found: C 76.27, 76.26; H 9.04, 9.03%. $C_{14}H_{20}O_2$. Calculated: C 76.41; H 9.16%.

Boiling with acetic anhydride under the conditions described previously [1] gave, from 65 g of 2-(β -cyclohexylideneethyl) dihydroresorcinol (II), 39 g of the enol acetate (IV), b.p. $134-137^{\circ}$ (0.05 mm); n_D^{20} 1.5190. Found: C 72.96, 73.25; H 8.40, 8.37%. $C_{16}H_{22}O_3$. Calculated: C 73.25; H 8.45%.

The 2,4-dinitrophenylhydrazone of the enol acetate of 2-(β -cyclohexylideneethyl) dihydroresorcinol melted at $160-161^{\circ}$ (from a mixture of methanol and dioxane). Found: N 12.84, 12.82%. $C_{22}H_{26}N_4O_6$. Calculated: N 12.65%.

By the action of an excess of ethereal diazomethane, 11 g of 2-(β -cyclohexylideneethyl) dihydroresorcinol gave 10.5 g of the O-methyl ether (III), b.p. $187-190^{\circ}$ (3 mm); m.p. $55-56^{\circ}$ (from hexane). Found: C 76.67, 76.47; H 9.42, 9.28%. $C_{15}H_{22}O_2$. Calculated: C 76.88; H 9.46%.

Ozonolysis of 2-(β -cyclohexylideneethyl) dihydroresorcinol. Ozonized oxygen (6% O_3) was passed for 1.5 hr, with cooling in ice-cold water, in a solution of 3 g of 2-(β -cyclohexylideneethyl) resorcinol in 60 ml of chloroform. In order to decompose the ozonides, the solution was boiled for 10 hr with 30 ml of a 5% solution of hydrogen peroxide with stirring. Four tenths of a gram of cyclohexanone (its 2,4-dinitrophenylhydrazone, m.p. $159-160^{\circ}$), and 0.9 g of glutaric acid were obtained.

Cyclization of 2-(β -cyclohexylideneethyl) dihydroresorcinol. A mixture of 3.2 g of 2-(β -cyclohexylideneethyl) dihydroresorcinol and polyphosphoric acid prepared from 5 g of anhydrous phosphoric acid and 5 g of phosphorus pentoxide was heated on a boiling water-bath for 2.5 hr. After dilution with water and neutralization with sodium carbonate, the reaction product was extracted with ether to give 2.3 g of 2-spirocyclohexyltetrahydrochroman-5-one (VI), b.p. $179-181^{\circ}$ (2 mm); m.p. $39-40^{\circ}$ (from hexane). Found: C 76.50, 76.58; H 9.36, 9.44%. $C_{14}H_{20}O_2$. Calculated: C 76.41; H 9.16%.

The 2,4-dinitrophenylhydrazone of (VI) melted at $189-190^{\circ}$ (from alcohol). Found: N 14.04, 14.08%. $C_{20}H_{24}O_5N_4$. Calculated: N 14.00%.

Reaction of the O-methyl ether of 2-(β -cyclohexylideneethyl) dihydroresorcinol with methyl magnesium iodide. A Grignard reagent prepared from 2.5 g of magnesium, 15 g of methyl iodide, and 50 ml of ether was treated, while stirring and cooling with ice, with 10.5 g of the O-methyl ether of 2-(β -cyclohexylideneethyl) dihydroresorcinol in 50 ml of ether. After the reaction mixture was allowed to stand at room temperature for 3 hr, it was treated with ice and dilute (1:1) hydrochloric acid. The ethereal solution was washed with dilute alkali and evaporated in vacuum to dryness. Distillation of the residue gave 4.5 g of the unsaturated ketone (V), b.p. $150-155^{\circ}$ (3 mm); n_D^{19} 1.5320. Found: C 82.19, 82.26; H 10.11, 10.15%. $C_{15}H_{22}O$. Calculated: C 82.51; H 10.16%.

The 2,4-dinitrophenylhydrazone of (V) melted at $137-138^{\circ}$ (from alcohol); λ_{max} 389 m μ (alcohol). Found: N 14.56, 14.61%. $C_{21}H_{26}O_4N_4$. Calculated: N 14.30%.

Attempts to cyclize the bicyclic unsaturated ketone (V). A mixture of 1.3 g of the bicyclic unsaturated ketone (V) and 8 ml of 85% phosphoric acid was left to stand for 24 hr at room temperature. The reaction mixture was diluted with water, neutralized with sodium carbonate, and extracted with ether. Upon cooling the ethereal solution with a mixture of dry ice and acetone, 0.6 g of the keto alcohol (XI) separated out, m.p. $66-67^{\circ}$ (from hexane). Found: C 76.02, 75.95; H 10.23, 10.10%. $C_{15}H_{24}O_2$. Calculated: C 76.22; H 10.24%.

The 2,4-dinitrophenylhydrazone of (XI) melted at $153-154^{\circ}$ (from alcohol); λ_{max} 390 m μ (alcohol). Found: N 13.63, 13.71%. $C_{21}H_{28}O_5N_4$. Calculated: N 13.46%.

Analogous results were obtained when the reaction was carried out at 100° (2-3 hr).

A mixture of 4.6 g of the unsaturated ketone (V) and polyphosphoric acid, prepared from 8 g of anhydrous phosphoric acid and 8 g of phosphorus anhydride, was heated on a boiling water bath for 3 hr. After the usual treatment, about 1 g of the keto alcohol (XI) with m.p. $64-66^{\circ}$ was separated out, together with a considerable amount of tarry products.

Hydrolytic fission of 2-(β -cyclohexylideneethyl)dihydroresorcinol. A mixture of 7 g of 2-(β -cyclohexylideneethyl)dihydroresorcinol and 15 g of barium hydroxide in 100 ml of water was refluxed for 10 hr. The solution was acidified with dilute hydrochloric acid; the oily mixture which separated out was extracted with ether. Cooling of the ethereal solution with dry ice gave 1.3 g of the keto acid (VII), m.p. 42-43° (from hexane). Found: C 70.28, 70.39; H 9.29, 9.16%. $C_{14}H_{22}O_3$. Calculated: C 70.55; H 9.31%.

Fractional distillation of the mother liquor led to the isolation of 3.5 g of the keto acid (VIII), b.p. 210-220° (2 mm). Found: C 70.41, 70.62; H 9.21, 9.32%. $C_{14}H_{22}O_3$. Calculated: C 70.55; H 9.31%.

By vacuum distillation (2 mm), the crystalline keto acid (VII) undergoes isomerization to the liquid isomer (VIII).

Ozonolysis of the crystalline keto acid (VII). Ozonized oxygen (6% O_3) was passed at 5-10° for 2 hr in a solution of 3.9 g of the crystalline keto acid (VII) in 60 ml of 90% acetic acid. To decompose the ozonides, the solution was mixed with 5 ml of a 20% solution of hydrogen peroxide, left to stand for 3 hr at room temperature, and distilled to dryness in vacuum (100°, 10 mm). Cyclohexanone was detected in the distillate by the formation of its 2,4-dinitrophenylhydrazone.

Ozonolysis of the liquid keto acid (VIII). Ozonolysis of 4 g of the liquid keto acid (VIII) under the above stated conditions gave 2.4 g of 4,8-diketododecane-1,12-dicarboxylic acid (IX), m.p. 104-106° (from water). Found: C 58.34, 58.33; H 7.87, 7.98%. $C_{14}H_{22}O_6$. Calculated: C 58.73; H 7.71%.

Cyclization of the keto acid (VIII). A mixture of 3 g of the liquid keto acid (VIII) and polyphosphoric acid prepared from 7 g of anhydrous phosphoric acid and 7 g of phosphorus anhydride was heated for 2 hr at 100°. Usual treatment led to 1.7 g of an oil, b.p. 160-170° (2 mm), which, upon solution in ether and cooling with dry ice gave 0.8 g of the aromatic ketone (XV), m.p. 77-78° (from hexane), λ_{max} 264.5 m μ (log 4.160) (alcohol). Found: C 83.88, 83.97; H 8.08, 8.20%. $C_{14}H_{16}O$. Calculated: C 83.96; H 8.05%.

The 2,4-dinitrophenylhydrazone of (XV) melts at 263-265° with decomposition (from alcohol), λ_{max} 391 m μ (alcohol). Found: N 14.86, 14.71%. $C_{20}H_{20}O_4N_4$. Calculated: N 14.60%.

Conversion of the aromatic ketone (XV) to phenanthrene-1-ol (XVI). One gram of the aromatic ketone (XV) and 1 g of 10% palladium on carbon was heated for 25 min at 280-300°. The cooled mixture was extracted with a hot 5% potassium hydroxide solution. Acidification of the alkaline solution with hydrochloric acid gave 0.3 g of phenanthrene-1-ol (XVI), m.p. 154-155° (from aqueous alcohol). Reported m.p., 156° [5].

Conversion of the aromatic ketone (XV) to 1-methylphenanthrene (XIII). A Grignard solution prepared from 0.1 g of magnesium and the corresponding amount of methyl iodide was treated, while cooling with ice and stirring, with 0.4 g of the aromatic ketone (XV). After leaving the reaction mixture to stand at room temperature for 3 hr, it was decomposed with ice and dilute hydrochloric acid. The ethereal solution yielded an oil which was heated for 20 min at 310-320° with 0.5 g of 10% palladium on charcoal. The cooled mixture was extracted with chloroform to give 1-methylphenanthrene (XIII), m.p. 121-122° (from alcohol); m.p. of the picrate, 137-138° (from alcohol). Reported m.p. 123°, and 139°, respectively [6].

SUMMARY

Hydrolysis of 2-(β -cyclohexylideneethyl)dihydroresorcinol (II) gives an unsaturated keto acid (VIII) which is converted by a double cyclization under the influence of polyphosphoric acid to 1-keto- $\Delta^{9,11,13}$ -octahydrophenanthrene (XV). This series of reactions can be useful for the synthesis of polycyclic compounds related to steroids.

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DEMETHYLATION OF METHYLCYCLOHEXANE
IN CONTACT WITH NICKEL CATALYSTS
UNDER HYDROGEN PRESSURE

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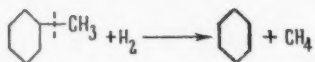
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One of the ways for preparing cyclohexane, on which is based at the present time the production of adipic acid, and, consequently, of nylon, is the catalytic hydrogenolysis of the side groups in alkylcyclohexanes, and in particular, in methylcyclohexane.



As the different varieties of petroleum of the Caucasus type have a high methylcyclohexane content, a smooth elimination of the methyl group from a methylcyclohexane molecule may have a practical interest. However, one can foresee considerable difficulties for the effective accomplishment of this reaction, as practically all the catalysts for the hydrogenolysis of C-C bonds are at the same time, to various degrees, catalysts for the dehydrogenation of the hexamethylene ring. Therefore, one of the aims of this work was to find appropriate catalysts and favorable conditions for the hydrogenolysis of the bond between the ring and the methyl group, the use of which would not render the dehydrogenation reaction of the hexamethylene ring predominant.

In 1937, one of us [1] has shown that when methyl- and dimethylcyclohexanes are passed through a layer of nickel-aluminum oxide catalyst at 330-360° under ordinary pressure in a current of hydrogen, methyl groups are eliminated from the starting cyclohexanes, as well as from their dehydrogenation products. Demethylation of methylcyclohexane on a skeletal nickel-cobalt-aluminum catalyst has also been detected by Sil'chenko [2]. During a study of the catalytic properties of finely dispersed platinum, palladium, ruthenium and rhodium deposited on aluminum oxide and silicon oxide, one of us has shown [3] that at 460° and 20-50 atm. of hydrogen, dehydrogenation is accompanied by a partial demethylation of methylcyclohexane. However, in the mentioned works, demethylation of methylcyclohexane was observed only as a side-reaction, and the selective action of the formerly studied catalysts has not been investigated from the point of view which interests us here. During the past few years, there appeared in the literature, as a result of the increasing demand for benzene, a series of patents and papers devoted to the demethylation of the aromatic hydrocarbons [4-8]. Thus, one of us [7,8] has investigated the selective demethylation of toluene to benzene on a nickel-aluminum oxide catalyst at high temperatures and high hydrogen pressure.

In the present work we are able to show that of the five nickel catalysts we have investigated, the most effective demethylating agent for methylcyclohexane is the nickel-aluminum oxide catalyst pretreated with hydrofluoric acid. The reaction is carried out at 360° in a flowing system under a hydrogen pressure of 20 atm. However, in these experiments, the yield of cyclohexane obtained by one passage over the catalyst does not exceed 25.6% with respect to the catalyzate and 30.1% with respect to the converted methylcyclohexane.

EXPERIMENTAL

The following were used as catalyst carriers: a) Silica gel of factory make, with 1.5-2 mm grain-size, treated several times with dilute (1:1) hydrochloric acid, then washed with distilled water until it gave a negative test for chlorine ions, and finally dried and calcined at 500° for 3 hr; b) Aluminum oxide of the type A-2, preliminarily calcined at 500° for 3 hr; c) Industrial aluminosilicate from GrozNII, treated in the same manner as the silica gel. The specific area of these carriers prepared by the mentioned procedures was determined by the dynamic method [9,10]; the values obtained were 210, 270, and 255 sq.m./g for aluminum oxide, silicon oxide, and aluminosilicate, respectively.

The nickel-aluminum oxide, nickel-silicon oxide, and nickel-aluminosilicate catalysts were prepared by impregnating the corresponding carrier with a solution of nickel nitrate in such a way as to have 10% of nickel adsorbed on the catalyst. A second sample of a 10% nickel-aluminum oxide catalyst was prepared by the simultaneous precipitation of the corresponding nitrates. A third sample of the nickel-aluminum oxide catalyst was prepared by treating aluminum oxide with hydrofluoric acid (1% HF w.r. to the weight of Al_2O_3), heating the product in a muffle furnace at 500° for 3 hr, and then impregnating it with a solution of nickel nitrate in such a way as to have 10% of nickel w.r. to the weight of the catalyst. The catalysts thus prepared were reduced at 350° for 15 hr with electrolytic hydrogen.

TABLE 1. Properties of Methylcyclohexane Catalyzates

Catalyst		Temp., °C	Yield of liquid catalyzate (wt. %)	Properties of the catalyzates			
				n_D^{20}	d_4^{20}	content of aromatic hydrocarbons (% by wt.)	
						w.r. to the cat- alyzate	w.r. to the original methylcyclo- hexane
Ni—Al ₂ O ₃	№ 1	360	80,0	1,4360	0,7857	21,6	17,3
Ni—Al ₂ O ₃							
Precipitated	№ 2	360	83,0	1,4315	0,7768	9,0	7,5
Ni—Al ₂ O ₃ —HF	№ 3	360	79,0	1,4308	0,7738	13,2	10,4
Ni—SiO ₂	№ 4	330	63,0	1,4240	0,7628	8,4	5,4
Ni—Al, silicate	№ 5	335	68,5	1,4210	0,7559	6,5	4,4

TABLE 2. Properties of Light Fractions isolated From Methylcyclohexane Catalyzates

Catalyst	Boiling range (°C)	Yield (% by wt.)		Properties	
		w.r. to the catalyzate	w.r. to methylcyclohexane	n_D^{20}	d_4^{20}
Ni- Al_2O_3	—	—	—	—	—
Ni- Al_2O_3 precipitated	—	—	—	—	—
Ni- Al_2O_3 -HF	29—40	1,5	1,2	1,3590	0,6195
Ni- SiO_2	27,5—40	1,9	1,2	1,3572	0,6216
Ni-aluminum silicate	27,4—40	2,5	1,7	1,3567	0,6219

The methylcyclohexane used in the experiments was purified from traces of aromatic hydrocarbons by adsorption on silica gel, followed by distillation on a column having an efficiency equivalent to 40 theoretical plates. Its constants were: b.p. 100,3-100,9° (760 mm); n_D^{20} 1,4234 d_4^{20} 0,7694.

TABLE 3. Composition of Aromatic Hydrocarbons Isolated From Methylcyclohexane Catalyzates

Catalyst	Yield of aromatic hydrocarbons in % by wt. w.r. to methylcyclohexane	
	benz.	toluene
Ni- Al_2O_3	3,5	13,8
Ni- Al_2O_3 precipitated	traces	7,5
Ni- Al_2O_3 -HF	1,4	9,0
Ni- SiO_2	2,0	3,4
Ni-aluminosilicate	1,0	3,4

The experiments were carried out in a continuous flow apparatus [11], with a molar relation of hydrogen to starting methylcyclohexane equal to 4:1, the temperature being 330-360°, the space velocity, 0,2 hr⁻¹, and the hydrogen pressure, 20 atm.

The refractive index, specific gravity, and aromatic hydrocarbon content (by the sulfuric acid method) of the catalyzates were determined. After a preliminary treatment for the removal of the butane fraction (distillation of the light fraction of the catalyzate by heating to 40°), each catalyzate was submitted to absorption fractionation on silica gel. The naphthene-paraffin fraction was rectified on a column equivalent to 40 theoretical plates. The aromatic part of the catalyzate, and some of its fractions containing the naphthene-paraffin hydrocarbons were investigated by the methods of Raman spectra and gas-liquid phase chromatography. The gaseous products isolated were analyzed

by the chromothermographic method; they consisted basically of methane and hydrogen. The amounts of C₂-C₄ hydrocarbons did not exceed 3%. The results obtained during the catalytic treatment of methylcyclohexane are given in Tables 1-5.

TABLE 4. Properties of the Naphthene-Paraffin Fraction of Methylcyclohexane Catalyzates.

Catalyst and temperature of the expt.	Fraction	Boiling range (°C)	Yield, wt. %		Properties	
			w.r. to catalyzate	wt. to starting methylcyclohexane	n_D^{20}	d_4^{20}
Ni—Al ₂ O ₃ , 360°	I	40—80,3	7,6	6,1	1,3900	0,6982
	II	80,3—81,3	22,2	17,8*	1,4259	0,7778
	III	81,3—100,2	6,7	5,4	1,4172	0,7559
	IV	100,2—100,7	33,2	26,6	1,4232	0,7692
	Residue	—	4,1	3,3	—	—
Ni—Al ₂ O ₃ , precipitated 360°	I	65—79,5	3,1	2,7	1,4170	0,7345
	II	79,5—81,5	3,7	3,2*	1,4258	0,7779
	III	81,5—100,0	4,4	3,7	1,4200	0,7601
	IV	100,0—100,6	69,6	57,8	1,4231	0,7694
	Residue	—	4,8	4,0	—	—
Ni—Al ₂ O ₃ —HF, 360°	I	40—70	5,0	3,9	1,3790	0,6643
	II	70—80	3,5	2,8	1,4089	0,7348
	III	80—81,5	25,6	20,3*	1,4260	0,7783
	IV	81,5—99,7	6,9	5,4	1,4150	0,7461
	V	99,7—100,8	36,8	29,1	1,4230	0,7692
	Residue	—	4,3	3,4	—	—
Ni—SiO ₂ , 330°	I	40—80	9,8	6,2	1,3920	0,6966
	II	80—81,1	20,3	12,2*	1,4260	0,7780
	III	81,1—100,3	10,8	6,8	1,4175	0,7588
	IV	100,3—100,8	37,5	23,8	1,4232	0,7694
	Residue	—	6,6	4,2	—	—
Ni—aluminosilicate 335°	I	40—80	11,1	7,6	1,3905	0,6996
	II	80—81,5	9,8	6,7*	1,4258	0,7779
	III	81,5—89,6	6,2	4,2	1,4123	0,7476
	IV	89,6—92,0	3,8	2,6	1,4043	0,7296
	V	92—100	4,9	3,4	1,4125	0,7482
	VI	100—100,8	44,6	30,5	1,4231	0,7694
	Residue	—	5,7	3,9	—	—

*The yields of cyclohexane in % by wt. with respect to the methylcyclohexane which has reacted, were 25.4; 8.4; 30.1; 17.0, and 10.0, respectively.

TABLE 5. Composition of the Naphthene-Paraffin Fraction of Methylcyclohexane Catalyzates*

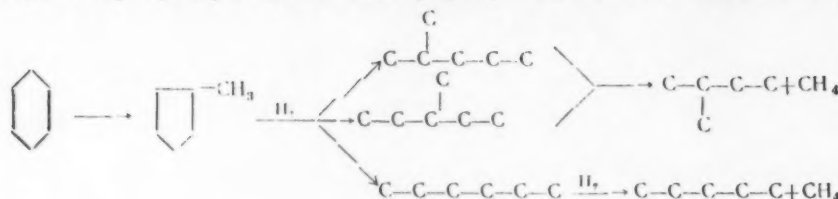
Boiling range (°C)	Hydrocarbon content in % by wt.	
	in the experiment with Ni—SiO ₂	in the experiment with Ni—Al ₂ O ₃ —HF
40-80	Isopentane 9.3	Isopentane 8.1
	n-pentane 6.7	n-pentane 2.8
	2-Methylpentane 17.2	2-Methylpentane 19.7
	3-Methylpentane 21.5	3-Methylpentane 16.1
	n-Hexane 13.3	n-hexane 15.4
	Methylcyclopentane 13.6	Methylcyclopentane 21.2
	Cyclohexane 18.4	Cyclohexane 16.7
81-100	—	Not less than 5 hydrocarbons with predominance of cyclohexane and methylcyclohexane

*This study has been carried out by the method of gas-liquid phase chromatography.

It follows from these data that the main reaction of methylcyclohexane on the samples of nickel-aluminum oxide catalysts studied (the first and third samples), under the given conditions, was its demethylation (Table 4), and to a lesser degree, its dehydrogenation to toluene. It is noteworthy that the best results were obtained with the nickel aluminum oxide catalyst pretreated with hydrofluoric acid. When this catalyst was used, the yield of cyclohexane was 30.1% with respect to the methylcyclohexane which had reacted. This catalyst is also the one which shows the greatest selectivity. Thus, with the mentioned yield of cyclohexane, the aromatic hydrocarbon content is only 10.4%, while the nickel-aluminum oxide catalyst which has not been pretreated with hydrofluoric acid gives only a 25.4% yield of cyclohexane, accompanied by a 17.3% aromatic hydrocarbon content.

The use of Ni-SiO₂ and nickel-aluminosilicate catalysts leads to the formation of a considerable amount of methane, and the yield of the catalyzate falls down to 63 and 68.5%, respectively; at the same time, the effluent gas contains 30-50% of methane. It is not excluded that the increase in the formation of gaseous products on the Ni-SiO₂ and Ni-aluminosilicate catalysts, as compared with the effect of the nickel-aluminum oxide catalyst, is due to the higher specific area of the former two carriers. The nickel-aluminum oxide catalyst obtained by precipitation was found to have a low activity for effecting the demethylation of methylcyclohexane under the chosen conditions.

As it appears from data in Table 5, the naphthene-paraffin fraction of methylcyclohexane catalyzates, obtained on the two nickel catalysts experimented with, contained, together with cyclohexane, some methylcyclopentane. This proves that there occurs a reaction with ring contraction, whereas the presence of normal alkanes and isoalkanes shows that there takes place a hydrogenolysis reaction of methylcyclopentane and of the alkanes themselves:



Analogous reactions also take place with methylcyclohexane.

SUMMARY

1. The catalytic demethylation of methylcyclohexane on nickel catalysts in a continuous system under a hydrogen pressure of 20 atm, and at 330-360° has been investigated.
2. The most effective catalyst for this reaction is the nickel-aluminum oxide catalyst obtained after a preliminary treatment of the carrier with hydrofluoric acid. The yield of cyclohexane treated on this catalyst is 30.1% per cycle, as calculated on the basis of the methylcyclohexane which has reacted.
3. The demethylation reaction of methylcyclohexane on nickel catalysts is somewhat complicated by the isomerization of a part of the cyclohexane produced to methylcyclopentane, with a subsequent hydrogenolysis of the latter, alkanes being formed.

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REACTION OF N₂O₄ WITH ORGANIC COMPOUNDS

COMMUNICATION 5. ARYL NITROLIC ACIDS; PREPARATION OF ARYLTRINITRO-METHANES THEREFROM; AND A ONE-STAGE SYNTHESIS OF ARYLTRINITROMETHANES FROM ARYL ALDOXIMES

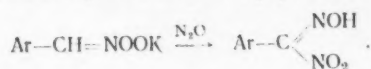
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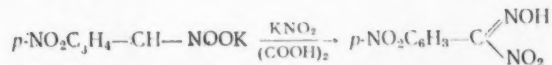
It was shown in the preceding communication [1] that aryl nitrolic acids can be converted in good yields to aryltrinitromethanes, which have been little investigated and are difficult to prepare*. Aryl nitrolic acids have also been comparatively little investigated, although several methods are known for their preparation. Benzonitrolic acid has been prepared by Wieland and Semper [3] by the acidification of a cooled solution of a mixture of the sodium salt of phenylnitromethane and sodium nitrite with oxalic acid. *m*-Nitro- and *p*-chlorobenzonitrolic acids have been prepared by Ruggeri [4] by the action of 0.5 M N₂O₄ on the corresponding aryl aldoximes in ethereal solution. We have found that aryl nitrolic acids are also obtained by the action of N₂O₄ on the salts of aryl nitromethanes [5]:



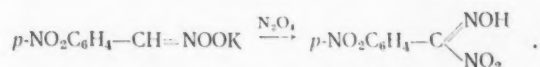
Finally, some aryl nitrolic acids have been prepared by the nitration of the corresponding oximes with fuming nitric acid [6].

By means of the first three methods, we prepared *p*-chloro-, *o*-nitro-, *m*-nitro-, and *p*-nitrobenzonitrolic acids. Further study has shown that aryl nitrolic acids can exist in two forms differing from each other in physical and some chemical properties. Depending on the method of preparation, either the one or the other form may be obtained, or a mixture of both forms. These phenomena have been the object of especially detailed study in the case of *p*-nitrobenzonitrolic acid.

The first form (I) of *p*-nitrobenzonitrolic acid appears as a pale yellow crystalline substance melting at 60-61° (with decomposition). It is easily soluble in aqueous alkali metal hydroxides and carbonates with the formation of the bright red-orange coloration which is characteristic for nitrolic acids. Its alkaline solution gives, upon treatment with benzoyl chloride, a precipitate of the benzoyl derivative. This form of *p*-nitrobenzonitrolic acid is formed when a solution containing the potassium salt of *p*-nitrophenylnitromethane and potassium nitrite is acidified with oxalic acid:



The second form (II) of *p*-nitrobenzonitrolic acid occurs as almost colorless crystals melting at 52-53°. Upon treatment with a solution of aqueous alkali metal hydroxide or carbonate, this form is immediately converted into a high melting product, without passing into solution, but giving a faint, rapidly fading yellow color at the moment when it comes in contact with the alkali. This form is obtained by the action of N₂O₄ on a suspension of the potassium salt of *p*-nitrophenylnitromethane in ether:



*Until now the only method for the preparation of aryl nitromethanes was the reaction between N₂O₄ and the salt of phenyldinitromethane [2].

If one tries to prepare p-nitrobenzonitrolic acid by the action of 0.5 M N_2O_4 on an ethereal solution of p-nitrobenzaldoxime, one obtains a difficultly separable mixture of the two forms of nitrolic acids.

m-Nitrobenzonitrolic acid, when prepared by the first two methods [1], is obtained only in the form I. When prepared from the corresponding oxime, this acid, as well as the p-chlorobenzonitrolic acid are obtained as a mixture of both forms.

By repeated crystallization of the mixture of the two forms of p-chlorobenzonitrolic acid, it is possible to separate the form II (m.p. 78-79°). Form I (m.p. 62-63°) has been obtained by us by acidification of an alkaline solution of the mixture of the two forms after filtration from the decomposition products of the form II. o-Nitrobenzaldoxime gives with N_2O_4 only the form I of nitrolic acid. The existence of two forms of aryl nitrolic acids can be explained on the grounds of syn-anti isomerism.

The melting points of the aryl nitrolic acids we have prepared, and those of their benzoyl derivatives are gathered in the following table:

TABLE

Acid	Form	M.p. (with dec.) °C	M.p. (with dec.) of the benzoyl deri- vatives, °C
p-Nitrobenzonitrolic	I	60-61	147-149
	II	48-50	-
p-Chlorobenzonitrolic	I	62-63	124-127
	II	78-79	-
m-Nitrobenzonitrolic	I	69-71	145
o-Nitrobenzonitrolic	I	77-78	137-139

In the present work, the conversion reaction of nitrolic acid into aryltrinitromethane in the presence of N_2O_4 has been studied on p-chloro-, o-nitro-, and p-nitrobenzonitrolic acids. It was established that both the p-chloro-, and the p-nitrobenzonitrolic acids (in forms I and II) give good yields of the corresponding aryltrinitromethanes when allowed to react with N_2O_4 . On the other hand, it was not possible to obtain o-nitrophenyltrinitromethane by the action of N_2O_4 on o-nitrobenzonitrolic acid. This is apparently due to the fact that a nitro group in o-position exerts a steric hindrance preventing the formation of the trinitromethyl group.

On the basis of the data obtained, we elaborated a method for the one-stage synthesis of aryltrinitromethanes from aryl aldoximes. The method consists essentially in the addition of N_2O_4 in two steps: the first portion of N_2O_4 is added under the conditions ensuring the maximum yield of nitrolic acid, and the second portion under the optimum conditions for the conversion of nitrolic acid into aryltrinitromethane.

EXPERIMENTAL

Preparation of p-nitrobenzonitrolic acid (in form II) by the action of N_2O_4 on the potassium salt of p-nitrophenyltrinitromethane. A suspension of 3 g of the potassium salt of p-nitrophenylmethane in 30 ml of absolute ether cooled to 3° was treated with 9 g of N_2O_4 (8M for 1M of salt), in one portion. The temperature of the reaction mixture rose rapidly to 20°, and effervescence took place at the same time. The reaction mixture was filtered from inorganic salt, washed with water and evaporated at room temperature. The crystals of p-nitrobenzonitrolic acid, which separated out, were washed on the filter with three 2 ml portions of chloroform, and then air-dried. Yield, 1.8 g (67%). After reprecipitation with hexane from a dichloroethane solution, the substance appeared as colorless needles melting at 52-53° (dec.), easily soluble in ether, somewhat less soluble in dichloroethane, and sparingly soluble in petroleum ether and hexane. Found: C 39.86; 39.87; H 2.42; 2.51; N 20.04; 19.97%. $C_7H_5N_3O_5$. Calculated: C 39.81; H 2.39; N 19.91%.

This substance decomposed instantaneously upon its introduction into a 10% aqueous solution of potassium hydroxide, or a 10% aqueous sodium bicarbonate solution, without passing into solution, and giving a weak, rapidly fading yellow color at the moment when it came in contact with alkali. Therefore, it was not possible to prepare its benzoyl derivative.

By the same procedure, we have prepared earlier [1] m-nitrobenzonitrolic acid (form I) with a 67% yield.

Preparation of p-nitrobenzonitrolic acid (in its I form) by the action of oxalic acid on a solution of a mixture of the potassium salt of p-nitrophenylnitromethane and potassium nitrite. To a solution of 10 g of the potassium salt of p-nitrophenylnitromethane in 400 ml of water cooled to 0 deg were added, in succession, a solution of 10 g of potassium nitrite in 40 ml of water, and a solution of 15 g of oxalic acid in 200 ml of water, the latter two solutions being first cooled to 0 deg. The precipitate which separated out was filtered off, twice washed with water, and treated on the filter with 20 ml of ether. The ethereal solution of p-nitrobenzonitrolic acid was then filtered to remove a little amount of insoluble substance (potassium oxalate), dried, and treated with 40 ml of hexane. The solution was then evaporated at room temperature under ordinary pressure, losing thereby most of its ether. The crystals which appeared in the solution were filtered off, washed with hexane, and air-dried at room temperature. The yield of crude p-nitrobenzonitrolic acid was 7 g (78%). After being twice reprecipitated with hexane from its dichloroethane solution, this substance melted at 60-61 deg (dec.); the m.p. did not change upon further reprecipitation. Found: C 40.21, 40.08; H 2.53; 2.50; N 19.83; 19.76%. $C_{17}H_5N_3O_5$. Calculated: C 39.81; H 2.39; N 19.91%.

When p-nitrobenzonitrolic acid was introduced into a 10% aqueous potassium hydroxide solution, it dissolved completely with the formation of the characteristic red-orange color. Like p-chloro- and m-nitrobenzonitrolic acids [4], p-nitrobenzonitrolic acid gives with benzoyl chloride in alkaline solution a good yield of O-benzoyl-p-nitrobenzonitrolic acid, m.p. 146-149° (pale yellow prisms, readily soluble in dichloroethane and chloroform, and sparingly soluble in alcohol). Found: N 13.30; 13.24%. $C_{14}H_9N_3O_6$. Calculated 13.39%.

In the same way we have already prepared [1] m-nitrobenzonitrolic acid (form I) with 84% yield.

Preparation of arylnitrolic acids by the action of N_2O_4 on arylalldoximes. For the preparation of p-nitrobenzonitrolic acid, a solution of 10 g of p-nitrobenzaldehyde in 100 ml of absolute ether, cooled to 0°, was treated with 2.75 g of N_2O_4 (0.5 M for 1 M of oxime). The reaction mixture turned green and a flocculent precipitate appeared. After 1 hr the mixture was removed from the cooling bath. The precipitate (0.2 g) was filtered off; the filtrate was washed with water, mixed with 150 ml of hexane, filtered again, and left to evaporate at room temperature in an open crystallizing dish. The crystalline product, which separated out (6 g, 47%), was a mixture of the two forms of p-nitrobenzonitrolic acid. When this product was introduced into a 10% aqueous potassium hydroxide solution, a part of it (form I of the nitrolic acid) dissolved with the formation of the characteristic red-orange color, while the remaining part (form II) underwent decomposition. Acidification of the alkaline solution with hydrochloric acid led to the decomposition of the form I of the nitrolic acid; however, addition of benzoyl chloride to the alkaline solution led to the separation of a precipitate of the benzoyl derivative, m.p. 147-149°, which did not give a melting point depression with the benzoyl derivative of p-nitrobenzonitrolic acid obtained by acidification of a solution containing the potassium salt of p-nitrophenylnitromethane and potassium nitrite with oxalic acid. That the reaction product was a nitrolic acid was also confirmed by the fact that it reacted with N_2O_4 to give p-nitrophenyltrinitromethane (see below).

p-Chloro- and m-nitrobenzonitrolic acids were obtained from the corresponding oximes by the same method. After evaporation of the reaction mixture, the residue consisted of a mixture of the two forms of nitrolic acids, from which one could isolate forms I by the following method. A mixture of the two forms of nitrolic acids was introduced into a 10% aqueous potassium hydroxide solution cooled to 0°. The red-orange solution thus obtained was filtered from the precipitated decomposition products of form II of nitrolic acid, and the filtered solution was acidified with 5% aqueous hydrochloric acid at 0°. The precipitate formed was filtered off, washed with water, and dried at room temperature. This gave forms I of m-nitrobenzonitrolic acid, and p-chlorobenzonitrolic acid with the respective yields of 40% and 39%.

After reprecipitation with hexane from its dichloroethane solution, m-nitrobenzonitrolic acid melted at 69-71° (dec.), and did not depress the melting point of the m-nitrobenzonitrolic acid obtained by the action of N_2O_4 on the potassium salt of m-nitrophenylnitromethane [1].

p-Chlorobenzonitrolic acid, after reprecipitation with hexane from its dichloroethane solution, melted at 62-63°- its m.p. did not change upon further purification by reprecipitation. Found: C 41.87; 42.02; H 2.60; 2.59; N 13.99; 14.25%. $C_7H_5N_2O_3Cl$. Calculated: C 41.90; H 2.51; N 13.97%.

Under the action of benzoyl chloride in the presence of alkali, p-chlorobenzonitrolic acid was smoothly converted into its benzoyl derivative, m.p. 124-127°. Found: C 55.00; 55.08; H 2.88; 2.98; N 9.22; 9.19%. $C_{14}H_9N_2O_4Cl$. Calculated: C 55.19; H 2.98; N 9.20%. Reported for the benzoyl derivative of p-chlorobenzonitrolic acid: m.p. 115°[4].

Form II of p-chlorobenzonitrolic acid was isolated in the following manner. After addition of N_2O_4 , and standing for 1 hr, the reaction mixture was filtered from the precipitate, which separated out (0.2 g), was washed with water, treated with 200 ml of heptane, and evaporated at room temperature in an open crystallizing dish. Crystals started to separate out while the solvent was evaporating. The mixture was filtered from time to time to remove the successive crops, consisting of two crystalline substances (pale yellow needles, and colorless leaflets). When almost all the ether had evaporated, leaving a hexane solution, the latter yielded only leaflets of the colorless substance. In this way, 5 g of a mixture of crystals, m.p. 68-72° (dec.) was obtained, together with 1.5 g of the colorless substance, m.p. 76-78° (dec.). The total yield was 6.5 g (50%). The colorless substance appeared to be form II of p-chlorobenzonitrolic acid. In the same way as form II of p-nitrobenzonitrolic acid, this substance immediately decomposed upon introduction into a 10% potassium hydroxide solution, without dissolving, but giving a rapidly fading yellow color at the moment when it was put in contact with alkali. After recrystallization from n-hexane, form II of p-chlorobenzonitrolic acid melted at 78-79° (dec.); its m.p. remained unchanged upon further recrystallization. Found: N 13.58; 13.72%. $\text{C}_7\text{H}_5\text{N}_3\text{O}_3\text{Cl}$. Calculated: N 13.97%. Reported m.p. of p-chlorobenzonitrolic acid, 78-79° [4].

Form II of m-nitrobenzonitrolic acid could not be isolated in this way from its mixture with form I; however, its presence was revealed by the formation of insoluble decomposition products upon treatment with alkali.

For the preparation of o-nitrobenzonitrolic acid, a solution of 4 g of o-nitrobenzaloxime in 40 ml of absolute ether was treated with 2.2 g of N_2O_4 (1 M for 1 M of oxime). The reaction mixture was filtered from the little precipitate formed, washed with water, and evaporated in an open dish at room temperature. The residue contained 4.2 g (81%) of o-nitrobenzonitrolic acid. This substance, after being washed thrice with chloroform (3 ml portions), and reprecipitated from acetic acid solution by addition of water, melted at 77-78° (dec.); further reprecipitation did not change its m.p. Found: C 39.75; 39.93; H 2.45; 2.43; N 19.39; 19.50%. $\text{C}_7\text{H}_5\text{N}_3\text{O}_5$. Calculated: C 39.81; H 2.39; N 19.91%. Reported m.p. of o-nitrobenzonitrolic acid, 84° [6].

o-Nitrobenzonitrolic acid is completely soluble in 10% aqueous potassium hydroxide solution with the formation of the characteristic red-orange color, and is therefore, the form I of the nitrolic acid. An alkaline solution of o-nitrobenzonitrolic acid, upon treatment with benzoyl chloride, gives a good yield of the benzoyl derivative, m.p. 137-139°. Found: C 53.46; 53.17; H 2.95; 2.94; N 13.39; 13.57%. $\text{C}_{14}\text{H}_9\text{N}_3\text{O}_6$. Calculated: C 53.34; H 2.88; N 13.33%.

Preparation of aryltrinitromethanes by the action of N_2O_4 on aryl nitrolic acids. A solution of 1 g of nitrolic acid in 20 ml of dry dichloroethane was treated with 4.5 of N_2O_4 , and the mixture was rapidly heated to 60-70°. After washing with water and 10% aqueous sodium bicarbonate solution, the reaction mixture was evaporated in an open dish at room temperature. The residue (an oil) was treated with concentrated sulfuric acid in a separating funnel. If the given aryltrinitromethane was a solid substance, the product crystallized out in the funnel. The crystals obtained were washed with water and dried. If the aryltrinitromethane was a liquid, the substance, following treatment with concentrated sulfuric acid, was dissolved in ether. The ethereal extract was washed with water, and evaporated in an open dish at room temperature. The residue was then dried in a vacuum desiccator. The amounts of starting materials can be increased in this experiment without diminishing the yield. The following nitrolic acids were converted by this method to the corresponding aryltrinitromethanes:

p-Nitrobenzonitrolic acid (form I, m.p. 60-61°). Yield of p-nitrophenyltrinitromethane, 58%, m.p. 46-47° (from hexane). This substance did not depress the melting point of authentic p-nitrophenyltrinitromethane prepared by the action of N_2O_4 on the potassium salt of p-nitrophenylnitromethane.

p-Nitrobenzonitrolic acid (form II, m.p. 52-53°). Yield of p-nitrophenyltrinitromethane, 46%. p-Nitrophenyltrinitromethane (without further purification) was converted by heating with alcoholic potash into the potassium salt of p-nitrophenyldinitromethane. From the latter, p-nitrophenyldinitromethane was isolated, which was identified by the melting point of its mixture with an authentic sample of p-nitrophenyldinitromethane (no depression).

Mixture of the two forms of p-nitrobenzonitrolic acids, (obtained by the action of N_2O_4 on p-nitrobenzaloxime). Yield of p-nitrophenyltrinitromethane, 50%.

p-Chlorobenzonitrolic acid (form I, m.p. 62-63°). Yield of p-chlorophenyltrinitromethane, 77%. This substance, which has not been yet described in the literature, appears as a yellow oily liquid, m.p. 13°; n_D^{20} 1.5548; d_4^{20} 1.532; Found: MR 54.79; Calculated MR 52.90; Molecular refraction exaltation, 1.89. Found: C 32.40; 32.39; H 1.71; 1.82; Cl 13.20; 13.45; N 16.15; 16.13%. $\text{C}_7\text{H}_4\text{N}_3\text{O}_6\text{Cl}$. Calculated: C 32.14; H 1.54; Cl 13.55; N 16.07%.

Similarly to m-nitrophenyltrinitromethane [2], and p-nitrophenyltrinitromethane, p-chlorophenyltrinitromethane is converted by heating with alcoholic potash to the potassium salt of p-chlorophenyldinitromethane. From this salt,

by acidification, was isolated p-chlorophenyldinitromethane, m.p. 53-54°. It gave no melting point depression when mixed with an authentic sample of p-chlorophenyldinitromethane. Reported m.p. of p-chlorophenyldinitromethane, 55° [4].

p-Chlorobenzonitrolic acid (form II, m.p. 78-79°). Yield of p-chlorophenyltrinitromethane, 75%. By heating with alcoholic potash it was converted into the potassium salt of p-chlorophenyldinitromethane. p-Chlorophenyldinitromethane was isolated from this salt, and identified by the m.p. of its mixture with an authentic sample of p-chlorophenyldinitromethane (no depression).

Preparation of aryltrinitromethanes by the action of N_2O_4 on aryl aldoximes. A solution of 10 g of the aryl aldoxime in 100 ml of absolute ether cooled to 0° was treated with N_2O_4 (0.5 M for 1 M of oxime). After 1 hr, the reaction mixture was removed from the cooling bath, filtered from some precipitated material, and the solution thus obtained was treated with 100 ml of dry dichloroethane, and 20 g of N_2O_4 . Then, the reaction mixture was rapidly heated to 50°, allowing the greater part of ether and the excess of nitrogen oxides to evaporate. The cooled reaction mixture was then treated in the same manner as for the preparation of aryltrinitromethanes from arylnitrolic acids. The following oximes have been converted into the corresponding aryltrinitromethanes by this procedure:

m-Nitrobenzaldoxime. Yield of m-nitrophenyltrinitromethane, 60%, m.p. 64° (from alcohol). It did not give a melting point depression when mixed with an authentic sample of m-nitrophenyltrinitromethane.

p-Nitrobenzaldoxime. Yield of p-nitrophenyltrinitromethane, 45%, m.p. 46-47° (from hexane). It did not give a melting point depression when mixed with an authentic sample of p-nitrophenyltrinitromethane.

p-Chlorobenzaldoxime. Yield of p-chlorophenyltrinitromethane, 49%, m.p. 13°. n_D^{20} 1.5546. By heating with alcoholic potash, it was converted into the potassium salt of p-chlorophenyldinitromethane. Acidification of an aqueous solution of this salt with hydrochloric acid gave p-chlorophenyldinitromethane, which was identified by its mixed melting point with an authentic sample of p-chlorophenyldinitromethane (no depression).

SUMMARY

1. A new method has been found for the preparation of aryl nitrolic acids, namely, the action of N_2O_4 on the salts of arylnitromethanes.
2. Aryl nitrolic acids exist in two forms.
3. The reaction of m-nitrobenzonitrolic acid with N_2O_4 to give a trinitromethyl derivative, which we have discovered earlier, is now extended to p-nitro- and p-chlorobenzonitrolic acids.
4. A one-stage method is proposed for the synthesis of aryltrinitromethanes from aryl aldoximes.

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A NEW METHOD FOR THE SYNTHESIS OF β -HALONITROALKANES

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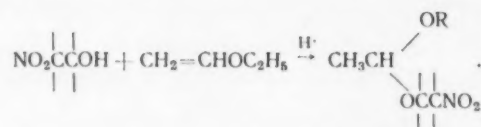
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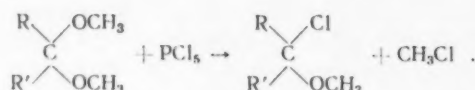
pp. 2026-2031, November, 1960

Original article submitted June 17, 1959

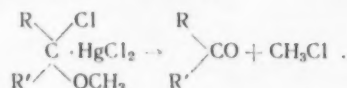
While studying the chemical reactions of aliphatic β -nitro alcohols in one of our works, we carried out their addition to vinyl ethers [1]. In this way were obtained and characterized for the first time a series of acetaldehyde acetals containing nitro groups:



It is known [2] that under the action of phosphorus pentachloride on ketals there occurs the replacement of one alkoxy group by a chlorine atom:



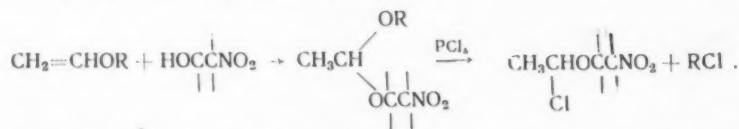
The α -chloro-substituted ethers thus obtained form complex compounds with mercuric compounds: the latter decompose upon heating to a ketone and an alkyl chloride [2]:



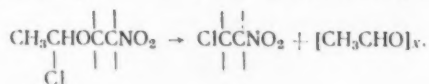
We decided to treat the acetals we had synthesized with phosphorus pentachloride, hoping to obtain in this way the β -chloronitroalkanes corresponding to the starting nitro alcohols.

Upon addition of these acetals to a mixture of phosphorus pentachloride and dry benzene, a strong evolution of heat was observed, accompanied by the gradual dissolution of phosphorus pentoxide. In order to complete the reaction it was necessary to heat the reaction mixture at 60-80° for a certain time. After distillation of benzene, a dark homogeneous mass was obtained. Heating of this reaction mass to 100° and higher led to effervescence and distillation of substances having a lower boiling point than the starting β -nitro alcohols. These substances are the corresponding β -chloronitroalkanes.

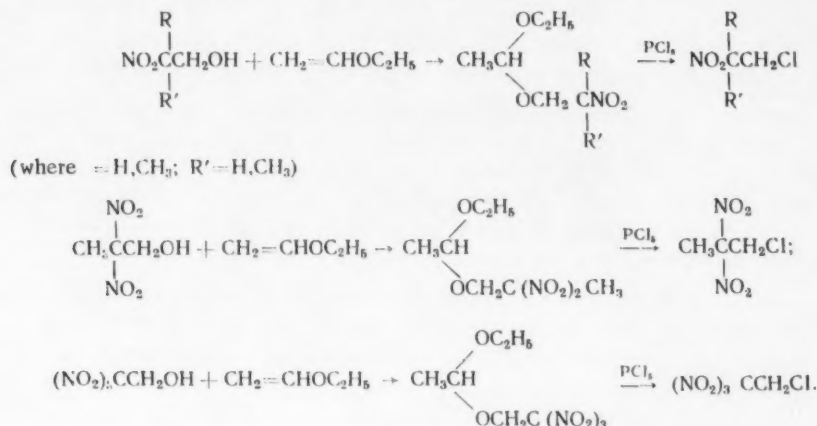
It is clear that just as in the case of ketals [2], the first step of the reaction is the replacement of the alkoxy group by a chlorine atom. It seems that the first to be thus replaced is the alkoxy containing no nitro group, as the reaction of phosphorus pentachloride with the *n*-butyl- β -nitroethylacetal of acetaldehyde [$\text{CH}_3\text{CH}(\text{OC}_4\text{H}_9\text{-n})\text{C}(\text{CH}_3)_2\text{OCCNO}_2$] without subsequent heating allows isolation of



The α -chloro- β -nitroethers which are formed in this case are probably thermally unstable; it was not possible to isolate them, as they already decompose at temperatures around 100°, with the formation of the corresponding β -chloronitroalkanes:

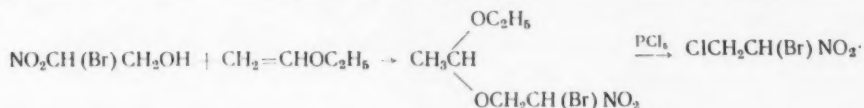


In this way, it is easy to convert to β -chloronitroalkanes the corresponding mononitro alcohols, dinitro alcohols, and trinitro alcohols, containing a primary hydroxyl group; this has been demonstrated in the cases of nitroethanol, 2-nitropropane-1-ol, 2-methyl-2-nitropropane-1-ol, 2,2,-dinitropropanol, and 2,2,2-trinitroethanol :

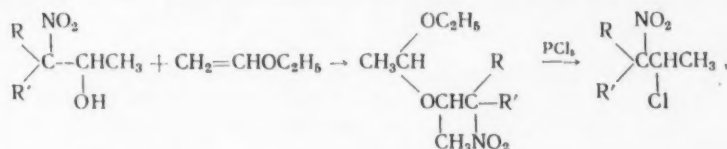


Cleavage of the ethyl- β -nitroethylacetal of acetaldehyde with thionyl chloride instead of phosphorus pentachloride also leads to the formation of β -chloronitroethane, but the latter is then obtained in smaller yield.

Similarly, 1-bromo-1-nitro-2-chloroethane has been synthesized from 2-bromo-2-nitroethanol:



No less easy is the formation of chloronitroalkanes from the corresponding nitro alcohols containing a secondary alcoholic group, such as 1-nitropropane-2-ol, 2-nitrobutane-3-ol, and 2-nitro-2-methyl-butane 3-ol:



where $\text{R} = \text{H}, \text{CH}_3$; $\text{R}' = \text{H}, \text{CH}_3$.

It appeared later that it is not necessary to isolate the acetals, as they could be made to react directly with phosphorus pentoxide.

EXPERIMENTAL

1-Chloro-2-nitroethane. This substance has been prepared by three methods:

1. Phosphorus pentachloride (9.4 g) and 15 ml of dry benzene were placed in a four-necked flask fitted with a mechanical stirrer, thermometer, reflux condenser, and dropping funnel. A solution of 7.4 g of ethyl- β -nitroethylacetal of acetaldehyde (b.p. 85-87°/4 mm) [1] in 10 ml of dry benzene was added with stirring during 5-10 min. The temperature rose gradually to 45-50°. The solution was stirred for 4 hr at room temperature, and left to stand overnight. After benzene was distilled off in vacuum, the residue was heated under reduced pressure (30-36 mm) on a boiling salt bath. There occurred a strong effervescence, and the chloride started to distil over. After a second vacuum distillation, the distillate gave 3.9 g (79%) of 1-chloro-2-nitroethane, b.p. 74-76° (20 mm); n_{D}^{20} 1.4510; d_4^{20} 1.3461. 1-Chloro-2-nitroethane, as well as all the other β -chloronitroalkanes prepared in this work, was purified prior

to analysis by carefully shaking the product with water, dissolving it in ether, and redistilling it after drying over magnesium sulfate. Found: C 22.37, 22.38; H 3.84; 3.97; N 12.91; 13.23; Cl 32.44; 32.18%. $C_2H_4NO_2Cl$. Calculated: C 21.92; H 3.65; N 12.79; Cl 32.42%. Reported [3]: B.p. 173-174°; d_4^{20} 1.405.

2. A mixture of 37 g of phosphorus pentachloride and 30 ml of dry benzene was treated, while stirring, with a solution of 28 g of undistilled ethyl- β -nitroethylacetal of acetaldehyde (prepared by the addition of 18 g of nitroethyl alcohol to vinyl ethyl ether with the subsequent removal of low-boiling products by distillation) in 20 ml of dry benzene. The rate of addition was regulated in such a way as to prevent the temperature of the reaction mixture rising above 60°. After the exothermal reaction was over, the reaction mixture was stirred for 1 hr at 50-60°, and distilled. The distillate gave, after a second fractionation, 16.9 g (77%) of 1-chloro-2-nitroethane, b.p. 72-75° (19 mm).

3. A stirred solution of 15.5 g of undistilled ethyl- β -nitroethylacetal of acetaldehyde (prepared from 9 g of nitroethanol) in 15 ml of dry benzene was treated with 25 g of thionyl chloride added at such a rate as to prevent the temperature of the reaction mixture rising above 40°. The solution was then stirred for 1.5 hr at 65-70°, and the low-boiling substances were removed in vacuum (water-pump). The residue was refluxed for 1 hr at 130-145°, cooled, and carefully extracted with ether. The ethereal solution was washed with water, dried with magnesium sulfate and distilled to give 5.9 g (54%) of 1-chloro-2-nitroethane, b.p. 72-76° (18 mm).

1-Chloro-2-nitropropane. A mixture of 17.3 g of 2-nitropropanol and 0.5 ml of absolute ether saturated with dry hydrogen chloride was treated, while stirring and keeping the temperature below 25°, with 25 ml of vinyl ethyl ether. Then, the mixture was heated for 1 hr at 50-60°, and the solution thus obtained was divided into two equal parts. The first part was distilled giving 8.8 g (60%) of ethyl- β -nitropropylacetal of aldehyde, b.p. 85-87° (7 mm), 99-100° (10 mm); n_D^{20} 1.4252; d_4^{20} 1.0511. Found: C 47.14; 47.22; H 8.28; 8.36%. $C_7H_{15}NO_4$. Calculated C 47.46; H 8.47%.

The second part of the reaction mixture was distilled to remove the low-boiling components, and the residue thus obtained was dissolved in 15 ml of dry benzene. This solution was treated, while stirring, with 15 ml of phosphorus pentachloride, and 15 ml of dry benzene at such a rate as to keep the temperature of the reaction mixture below 50°. After stirring for 1 hr at 50-60°, the reaction mixture was distilled. After three fractionations, 6.3 g (61%) of 1-chloro-2-nitropropane was obtained, b.p. 53-54° (7 mm); n_D^{20} 1.4450; d_4^{20} 1.2418. Reported [4]: b.p. 65-68° (10 mm); [5] d_4^{18} 1.2.

1-Chloro-2-nitro-2-methylpropane. A mixture of 35.7 g of 2-nitro-2-methylpropane-1-ol and 0.5 ml of absolute ether saturated with dry hydrogen chloride was treated, while stirring and keeping the temperature below 25°, with 40 ml of vinyl ethyl ether. After heating for 1 hr at 50-60°, the solution was divided into two equal parts. One part was distilled, giving 14.6 g (51%) of ethyl- β -nitro- β -methylpropyl acetal of acetaldehyde, b.p. 82-90° (2 mm); n_D^{20} 1.4348; d_4^{20} 1.0663. Found: C 50.65; 50.86; H 8.16; 8.28%. $C_8H_{17}NO_4$. Calculated: C 50.79; H 7.99%.

The second part was freed from low-boiling products by distillation. A solution of the residue in 15 ml of dry benzene was then treated with 32 g of phosphorus pentachloride, while stirring and keeping the temperature below 50°. After stirring for 1 hr at 50-60°, the reaction mixture was distilled. Thrice repeated distillation gave 5.2 g (25%) of 1-chloro-2-nitro-2-methylpropane b.p. 62-65° (10 mm); n_D^{20} 1.4476; d_4^{20} 1.2243; Found: C 34.42; 34.68; H 5.79; 5.93; Cl 26.44; 26.57%. $C_4H_8NO_2Cl$. Calculated C 34.91; H 5.82; Cl 26.82%. Reported [6]: b.p. 181-183°; n_D^{19} 1.4446; d_4^{19} 1.1822.

1-Chloro-2,2-dinitropropane. A mixture of 5.7 g of phosphorus pentachloride and 15 ml of dry benzene was treated, while stirring, with a solution of 6 g of ethyl- β , β -dinitropropylacetal of acetaldehyde [b.p. 96-99° (4 mm)] [1] in 25 ml. The addition was done in 5 min. After the exothermal reaction was over the reaction mixture was heated with stirring for 4 hr, and distilled at a bath temperature below 110°. Repeated distillation gave 2.6 g (57%) of 1-chloro-2,2-dinitropropane, b.p. 63-65° (4 mm); 60-61° (2 mm); n_D^{20} 1.4586; d_4^{20} 1.4367. Found: C 21.68, 21.72; H 3.14, 3.23; N 16.28, 16.31; Cl 21.42, 21.60%. $C_3H_5N_2O_4Cl$. Calculated: C 21.36; H 3.97; N 16.61; Cl 21.68%. Reported [7]: B.p. 200-202° (dec.); 103-105 (15.4 mm);

A mixture of 21 g of phosphorus pentachloride and 25 ml of dry benzene was treated, while stirring, with a solution of 25 g of undistilled ethyl- β , β -dinitropropylacetal of acetaldehyde (prepared from 16 g of 2,2-dinitropropanol) [1] in 25 ml of dry benzene at such a rate as to keep the temperature of the reaction mixture below 60°. After heating at 50-60° for 1 hr, the reaction mixture was distilled at a bath temperature below 110°, giving 11.7 g (65%) of 1-chloro-2,2-dinitropropane, b.p. 70-73° (2 mm).

1-Chloro-2,2,2-trinitroethane. A mixture of 15 g of phosphorus pentachloride and 10 ml of dry benzene was treated, while stirring, with a solution of 18 g of undistilled ethyl β, β, β -trinitroethylacetal of acetaldehyde (obtained from 13.5 g of trinitroethyl alcohol) [1] in 10 ml of dry benzene. The addition took 10 min. The mixture was boiled for 30 min, and distilled under reduced pressure in an atmosphere of nitrogen at a bath temperature below 110°. After a second distillation, 6.1 g (40%) of 1-chloro-2,2,2-trinitroethane was obtained, boiling at 59-61° (4 mm); 52-56° (3 mm); n_D^{20} 1.4668; d_4^{20} 1.5673. Found: C 12.25, 12.34; H 0.94; 1.00; N 20.91; 20.78; Cl 17.78, 17.73 $C_2H_2N_3O_6Cl$. Calculated: C 12.03; H 1.00; N 21.05; Cl 17.79%.

1-Bromo-1-nitro-2-chloroethane. For the preparation of 2-bromo-2-nitroethanol, a solution of 27.3 g of nitroethanol in 30 ml of absolute methanol was treated in portions, while stirring and keeping the temperature of the reaction mixture between -5° and 0°, with a solution of 6.95 g of sodium metal in 106 ml of absolute methanol. Then, the mixture was stirred for 2 hr at 0°. The precipitate, which separated out, was filtered off, washed with cold absolute methanol and absolute ether, and dried in a vacuum desiccator. The yield of the sodium salt of nitroethanol thus obtained was 32.8 g (93%). A suspension of 32.8 g of the sodium salt of nitroethanol in 210 ml of absolute ether was treated, while stirring and keeping the temperature between -2° and 0°, with 13.5 g of bromine. The addition required 1 hr. The reaction mass was stirred for a further hour at 0°; then, the precipitate was filtered off and washed with ether. The ethereal solution was evaporated in vacuum, and the residue submitted to fractional distillation. The yield of 2-bromo-2-nitroethanol thus obtained was 40.7 g (80%), b.p. 95-97° (8 mm). Reported in the literature [8]: b.p. 113° (15 mm).

2-Bromo-2-nitroethanol was made to react with vinyl ethyl ether as follows: a mixture of 40 g of 2-bromo-2-nitroethanol and 0.5 ml of absolute ether saturated with dry hydrogen chloride was treated, while stirring and keeping the temperature below 30°, with 30 ml of vinyl ethyl ether. After the exothermal reaction was over, the mixture was stirred for 1 hr at 50-60°, and then divided into two equal parts. The first part of the reaction product was distilled 17.8 g (60%) of ethyl- β -bromo- β -nitroethylacetal of acetaldehyde was thus obtained, b.p. 85-86° (3 mm); n_D^{20} 1.4790.

In order to prepare 1-bromo-1-nitro-2-chloroethane, a mixture of 22.3 g of phosphorus pentachloride in 10 ml of dry benzene was treated, while stirring and keeping the temperature below 70°, with the second part of the reaction mixture obtained in the preceding experiment, and preliminarily freed from low-boiling products under the vacuum produced with the help of a water-pump. The mixture was stirred at 50-60° for 1 hr, and distilled, giving 12.6 g (57%) of 2-bromo-2-nitro-1-chloroethane, b.p. 55-61° (8 mm); n_D^{20} 1.5023; d_4^{20} 1.5073. Found: C 13.60; 13.40; H 1.62; 1.68; N 7.36; 7.27%. $C_2H_3BrClNO_2$. Calculated C 12.73; H 1.59; N 7.42%.

Reaction of phosphorus pentachloride with the n-butyl- β -nitroethylacetal of acetaldehyde. Phosphorus pentachloride (10.2 g) was treated, while stirring and keeping the temperature below 30°, with 9 g of butyl- β -nitroethylacetal of acetaldehyde [b.p. 98-101° (4 mm)] [1]. The addition took 10 min. The reaction mixture was allowed to stand overnight, and then distilled. Butyl chloride [1.8 g, b.p. 45-50° (300-400 mm), n_D^{20} 1.3972] was the first to distill over. Upon stronger heating (above 80°), the mixture began to effervesce strongly, and 1-chloro-2-nitroethane [3.1 g, b.p. 75-78° (20 mm)] appeared in the distillate.

1-Chloro-1-nitropropane. A mixture of 20 g of phosphorus pentachloride and 14 ml of dry benzene was heated gradually and with stirring, with a solution of 12 g of undistilled ethyl- β -nitroisopropylacetal of acetaldehyde (prepared from 10.5 g of 1-nitropropane-2-ol) [1] in 15 ml of dry benzene. The reaction mixture was maintained below 60° by cooling in a bath. The mixture was stirred for 4 hr, and left to stand overnight. After two distillations, 8.5 g (69%) of 2-chloro-1-nitropropane was obtained, b.p. 82-48° (30 mm); 70-72° (20 mm); n_D^{20} 1.4455; d_4^{20} 1.2262. Found: C 29.07; 29.33; H 5.09; 5.00; Cl 28.38; 28.40%. $C_3H_6NO_2Cl$. Calculated: C 29.15; H 4.86; Cl 28.74%. Reported [4]: b.p. 56-58° (10 mm).

2-Chloro-3-nitrobutane. A mixture of 25 g of phosphorus pentachloride and 15 ml of dry benzene was treated, while stirring with a solution of 20.7 g of undistilled ethyl-(α -methyl- β -nitropropyl)acetal of acetaldehyde (prepared from 12.5 g of 3-nitrobutane-2-ol) [1] at such a rate as to keep the temperature of the mixture below 60°. The mixture was stirred at 60° for 1 hr, and distilled. After two distillations, 7.8 g (53%) of 2-chloro-3-nitrobutane was obtained, b.p. 68-72° (17 mm); n_D^{20} 1.4471; d_4^{20} 1.1829. Found C 35.31; 35.21; H 5.96; 6.00; Cl 26.48; 26.34%. $C_4H_8NO_2Cl$. Calculated C 34.91; H 5.82; Cl 26.82%.

2-Chloro-3-nitro-3-methylbutane. Thirty milliliters of vinyl ethyl ether was added, while stirring and keeping the temperature at 20-25°, to a mixture of 16.2 g of 3-nitro-3-methylbutane-2-ol and 0.5 ml of absolute ether saturated with dry hydrogen chloride. The reaction mixture was stirred for 1 hr at 50-60° and divided into two equal parts.

The first part was distilled to give 10.5 g (85%) of ethyl-(α , β -dimethyl- β -nitropropyl) acetal of acetaldehyde, b.p. 94-97° (8 mm); n_D^{20} 1.4310; d_4^{20} 1.0141. Found: C 52.31; 52.44; H 9.28; 9.20%. $C_9H_{19}NO_4$. Calculated: C 52.68; H 9.20%.

The second part was freed from low-boiling components by distillation, and the residue (12.5 g) was dissolved in 15 ml of dry benzene. The solution thus obtained was added to a mixture of 13 g of phosphorus pentachloride and 20 ml of dry benzene, while keeping the temperature below 60°. The mixture was stirred for 1 hr at 50-60°, and distilled. After two distillations, 3.8 g (41%) of 2-chloro-3-nitro-3-methylbutane was obtained, b.p. 58-62° (8 mm) n_D^{20} 1.4381. Found: C 40.09; 40.19; H 6.89; 6.90; Cl 23.82; 23.60%. $C_5H_{10}NO_2Cl$. Calculated: C 39.73; H 6.62; Cl 23.51%.

SUMMARY

A new method is elaborated for the synthesis of β -chloronitroalkanes; it consists in the reaction of phosphorus pentachloride with acetals obtained by the addition of primary β -nitro alcohols to vinyl alkyl ethers.

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ISOTOPE EXCHANGE REACTIONS OF HYDROGEN
IN ALKYL HALIDES

COMMUNICATION 1. HYDROGEN EXCHANGE OF TERTIARY BUTYL CHLORIDE
IN ANHYDROUS GLACIAL ACETIC ACID IN THE PRESENCE OF APROTONIC ACIDS

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We have already reported [1] our success in proving by the method of deuterium exchange that tertiary alkyl halides (chlorides, bromides, iodides) easily exchange their hydrogen atoms for the deuterium of anhydrous formic, hydrochloric and hydriodic acids, while no such hydrogen exchange is observed under similar conditions with secondary and primary alkyl halides. It was also established that tertiary chlorides do not participate in the reaction of hydrogen exchange with deutoacetic acid at room temperature, while tertiary bromides do participate in hydrogen exchange under the same conditions, but at a considerably lower rate than with formic acid. We supposed that the reaction of hydrogen exchange of alkyl halides is a consequence of their ionization, which depends on the dielectric constant of the medium, the nature of the halogen atom, and the constitution of the alkyl group.

In conformity with these assumptions, one could foresee that the hydrogen exchange of alkyl halides would be favored by the presence in the reaction medium of the salts of coordinationally unsaturated metals, such as AlCl_3 , FeCl_3 , and SnCl_4 , which, because of their electron-acceptor properties, expedite the heterolysis of the C-Halogen link in alkyl and acyl halides. To verify this supposition, we investigated the hydrogen exchange reaction of tert-butyl chloride in the presence of the salts of coordinationally unsaturated metals (aprotonic or Lewis acids), viz., FeCl_3 , SbCl_5 , ZnCl_2 , HgCl_2 , SnCl_4 , and BF_3 in deutoacetic acid medium. It appeared that tert-butyl chloride, which practically does not participate in the hydrogen exchange reaction with deutoacetic acid, exchanges all its hydrogen atoms in the presence of catalytic amounts of aprotonic acids, the rate of the hydrogen exchange of the alkyl halide depending to a considerable extent on the nature of these acids. Thus, tert-butyl chloride, which does not participate in hydrogen exchange with deutoacetic acid at 20° , underwent a slow exchange in the presence of mercuric chloride, and rapidly exchanged all its hydrogen atoms for deuterium in the presence of the same molar amount of FeCl_3 .

TABLE 1. Hydrogen Exchange of Tert-Butyl Chloride in Acetic Acid * in The Presence of Aprotonic Acids at 20°

Aprotonic acid	Molecular proportions			Velocity constants of the hydrogen exchange
	t-C ₄ H ₉ Cl	CH ₃ COOD	Aprotonic acid	
Without catalyst	1	10	0	No exchange
HgCl ₂	1	8.6	0.05	0.9
FeCl ₃	1	10	0.052	102
SbCl ₅	1	10	0.052	73
SnCl ₄	1	10	0.053	24
BF ₃ **	1	10	0.05	Practically no exchange
ZnCl ₂	1	9.9	0.10	8.1
LiCl	1	10	0.05	No exchange

* The hydrogen exchange was carried out in the presence of ~2% acetic anhydride

** A hydrogen exchange can be observed at 40° in the presence of 0.22 mol. of BF_3 per mole of $\text{C}_4\text{H}_9\text{Cl}$

In Table 1 are gathered data showing the influence of various aprotic acids on the rate of hydrogen exchange of tert-butyl chloride in deuterioacetic acid. For comparison, the same table gives data pertaining to hydrogen exchange in the presence of LiCl, which possesses only a rather weakly characterized coordinational unsaturation, and does not, practically, constitute a Lewis acid.

It follows from the given data that a particularly strong increase in the velocity of hydrogen exchange is imparted by ferric chloride and antimony pentachloride. It is significant that lithium chloride, which has only a rather weakly characterized coordinational unsaturation, does not catalyze the hydrogen exchange.

In order to compare the activity of various aprotic acids, we studied the kinetics of the hydrogen exchange of tert-butyl chloride at several different temperatures (20, 25, 30, and 40°), and with different amounts of catalysts. The results are given in Table 2. It appeared that with a temperature rise to 30-40°, a noticeable hydrogen exchange occurred with tert-butyl chloride even in the absence of a catalyst (Exp. 1, Table 2); however, the rate of this reaction was very low. At all the temperatures experimented with, the highest activity was displayed by FeCl₃ and SbCl₅, and the lowest by HgCl₂, while ZnCl₂ and SnCl₄ took an intermediate position.

TABLE 2. Hydrogen Exchange of Tert-Butyl Chloride in Deuterioacetic acid in the presence of Aprotic Acids

No. of expt.	Catalyst	Velocity constants of the hy- drogen exchange * K · 10 ⁴ sec ⁻¹				Activation energy Kcal/M
		20°	25°	30°	40°	
Molecular proportions: C ₄ H ₉ Cl: CH ₃ COOH: catalyst = 1:10:0.5						
1	Without catalyst	No ex- change	0,06	0,8	1,6	57
2	FeCl ₃	102	177	294	618	17
3	SbCl ₅	73	106	235	417	21
4	SnCl ₄	24	44	88	260	22
5	HgCl ₂	0,9	1,6	3,7	13,6	27
Molecular proportions = 1:10:0.1						
6	FeCl ₃	186	349	713	2170	25
7	SbCl ₅	151	311	717	1590	25
8	SnCl ₄	40	59	123	382	24
9	ZnCl ₂	8	16,5	28,5	109	26

*The given velocity constants of hydrogen exchange are a mean of 4-6 determinations.

We compared the values of the velocity constants of the hydrogen exchange of tert-butyl chloride in the presence of different aprotic acids with the same molecular proportions of the components by calculating the relative activities of these acids. The relative activities of the aprotic acids taken in the ratio of 5 mol % acid to alkyl chloride are tabulated in Table 3. The value of the velocity constant of the hydrogen exchange of tert-butyl chloride in the presence of mercuric chloride has been arbitrarily taken as equal to unity. Table 4 gives the values of the relative activities of aprotic acids when they participate in the reaction in the proportion of 10 mol % acid to alkyl chloride. In this case, the value of the velocity constant of hydrogen exchange of tert-butyl chloride in the presence of ZnCl₂ is taken to be equal to unity. Experiments with mercuric chloride have not been carried out at these concentrations because of the limited solubility of this salt in anhydrous acetic acid.

TABLE 3. Relative Activity of Aprotic Acids in Reactions of Hydrogen Exchange of Tert-Butyl in Acetic Acid. (Molecular proportions. - Chloride: CH₃COOH:MeCl_x = 1:10:0.05)

Aprotic acid	Rel. values of the velocity constants of hydrogen exchange K _{MeCl_x} /K _{HgCl₂}			Mean value K _{MeCl_x} /K _{HgCl₂}
	20°	25°	30°	
HgCl ₂	1	1	1	1
ZnCl ₂	5	8	7	7
SnCl ₄	27	28	31	29
SbCl ₅	81	76	82	80
FeCl ₃	114	125	103	114

From the data in Tables 3 and 4, it follows that the values of the relative activities of the various aprotic acids remain approximately constant in the temperature interval from 20-30° in the case of both the investigated concentrations.

On the basis of the data obtained, one can arrange the aprotic acids under discussion in the following sequence: FeCl₃ > SbCl₅ > SnCl₄ > ZnCl₂ > HgCl₂ > BF₃, according to their influence on

TABLE 4. Relative Activity of Aprotic Acids
($\text{MeCl}_x = 10 \text{ mol } \% \text{ of the wt of } t\text{-C}_4\text{H}_9\text{Cl}$)

MeCl_x	$K_{\text{MeCl}_x}/K_{\text{ZnCl}_2}$			Mean value $K_{\text{MeCl}_x}/K_{\text{ZnCl}_2}$
	20°	25°	30°	
ZnCl_2	1	1	1	1
SnCl_4	5	4	5	5
SbCl_5	19	19	26	21
FeCl_3	24	22	26	24

the velocity of hydrogen exchange of tert-butyl chloride. Their relative activities can be expressed, correspondingly, by the following numerical values: 114 : 80 : 29 : 7 : 1 for concentrations equal to 5 ml % of the weight of tert-butyl chloride. Our data concerning the activity of a series of aprotic acids in hydrogen exchange reactions of tert-butyl chloride are in concordance with the data of Jensen and Brown [2], who studied the kinetics of the benzylation of benzene derivatives in the presence of Friedel-Crafts catalysts. These authors have found that the different Friedel-Crafts catalysts can be placed in the following sequence: $\text{SbCl}_5 > \text{FeCl}_3 > \text{GaCl}_3 > \text{AlCl}_3 > \text{SnCl}_4 > \text{BCl}_3$ according to

their activity in the benzylation reactions. It follows that our data pertaining to the hydrogen exchange reaction of tert-butyl chloride in the presence of aprotic acids, as well as the literature data, are in conformity with the concept that the hydrogen exchange of tert-butyl chloride is conditioned by the heterolysis of the carbon to chlorine bond, and the formation of carbonium ions.

EXPERIMENTAL*

As starting materials we used tert-butyl chloride, b.p. 51°; n_D^{20} 1.3852; d_4^{20} 0.8439, obtained from tert-butyl alcohol by the action of hydrochloric acid. Deuteroacetic acid was obtained by the decomposition of acetic anhydride with water enriched with deuterium oxide. In the hydrogen exchange experiments we used an acid containing 1-2% of acetic anhydride. In some particular experiments we used an acid containing 5% of acetic anhydride. As aprotic acids, we used in our experiments chemically pure metallic chlorides, namely, FeCl_3 , SnCl_4 , SbCl_5 , HgCl_2 , ZnCl_2 , SnCl_4 , and SbCl_5 , which were additionally purified by vacuum distillation in a nitrogen atmosphere. Zinc chloride was fused to expel traces of moisture, and the molten salt was poured into acetic acid containing an excess of acetic anhydride. Chemically pure FeCl_3 and HgCl_2 were not submitted to additional purification.

Experiments on the hydrogen exchange of tert-butyl chloride were carried out in a deuteroacetic acid medium containing 1-2% of acetic anhydride. Weighed amounts of aprotic acids were introduced into acetic acid in an atmosphere of dry nitrogen inside a special chamber; the solution was then placed in a thermostat. Addition of tert-butyl chloride to the reaction medium, and removal of samples were also carried out in an atmosphere of dry nitrogen. Tert-butyl chloride was isolated from the samples by vacuum distillation at the temperature of the experiment. The distillation time (2-3 min) was taken into account in the kinetic calculations. In some experiments, the alkyl chloride was isolated from the reaction mixture by pouring the sample into ice-cold water. The two procedures gave approaching results. As all the kinetic experiments have been carried out under comparable conditions, we shall confine ourselves to the description of only two typical cases.

Hydrogen exchange of tert-butyl chloride in acetic acid in the presence of FeCl_3 . Ferric chloride (1.47 g, 9.1 mM) was dissolved in 53.53 g (892.1 mM) of deuteroacetic acid (9680 g/ml) containing 5.4% of acetic anhydride. The solution was placed in a thermostat at 30.2°, and tert-butyl chloride (8.35 g, 90.3 mM) was added. Every 10 min, 12-15 ml samples were removed from the reaction mixture; tert-butyl chloride was isolated from the samples by vacuum distillation at 30°. The chloride was treated with a 2-3% potassium hydroxide solution, washed with water, dried over CaCl_2 , and analyzed. The deuterium content was determined by the drop method. The following results were obtained:

No. of sample	Time (min)	Residual density of combustion water of tert-butyl chloride, g/ml			Mean value $K \cdot 10^5 \text{ sec}^{-1}$
		calculated	found	$K \cdot 10^5 \text{ sec}^{-1}$	
1	11	5050	235	7.20	7.13
2	20	5050	414	7.12	
3	30	5050	605	7.08	
4	41	5050	765	6.67	

*With the participation of A. N. Astakhov and L. E. Andreev.

Hydrogen exchange of tert-butyl chloride in acetic acid in the presence of SnCl_4 . Stannic chloride (2.56 g, 9.8 mM) was dissolved in 59.45 g (991 mM) of deuterioacetic acid (11210 γ/ml). The solution was placed in a thermostat at 20°, and tert-butyl chloride (8.59 g, 94 mM) was added. The samples were poured into ice-cold water, and the alkyl chloride layer was purified as described in the experiment with ferric chloride. The following results were obtained:

No. of sample	Time (min)	Residual density of combustion water of tert-butyl chloride, γ/ml		$K \cdot 10^4 \text{ sec}^{-1}$
		calculated	found	
1	120	6049	168	3,89
2	240	6049	330	3,89
3	360	6049	443	3,43
4	480	6049	738	4,51

It is necessary to note that in certain experiments (mostly with highly active catalysts at 30–40°), a gradual decrease of the values of the velocity of hydrogen exchange has been observed. We succeeded to prove that this phenomenon is conditioned by the accumulation of butyl acetate in the reaction mixture. Moreover, we found out that FeCl_3 gradually reacts with acetic acid with the formation of an insoluble complex compound corresponding to the composition: $\text{CH}_3\text{COOH} \cdot \text{FeCl}(\text{OH})(\text{OCOCH}_3)$. Apparently, SbCl_5 reacts in a similar manner. In order to reduce the possible errors, we studied the hydrogen exchange of tert-butyl chloride during the initial stage of the reaction, when the competing phenomena (formation of acetate, and alteration of the catalyst) have no practical importance. In such cases, however, we were obliged to work with acetic acid containing a relatively high amount of deuterium (corresponding to 10–12,000 γ/ml) in order to minimize the errors which might have occurred during the measurement of the isotopic composition of the combustion water of the tert-butyl chloride. On the other hand, in such cases, we carried out several parallel experiments and we calculated the mean value of the rate of hydrogen exchange.

SUMMARY

1. Tert-butyl chloride participates in a hydrogen exchange reaction with anhydrous deuterioacetic acid in the presence of the salts of coordinationally unsaturated metals, viz., FeCl_3 , SbCl_5 , SnCl_4 , ZnCl_2 , HgCl_2 . No hydrogen exchange is observed in the same medium in the absence of aprotic acids.
2. Kinetic studies show that the rate of exchange depends substantially on the nature of the aprotic acid. According to their influence on the rate of hydrogen exchange aprotic acids can be arranged in the following sequence: $\text{FeCl}_3 \approx \text{SbCl}_5 > \text{SnCl}_4 > \text{ZnCl}_2 > \text{HgCl}_2 > \text{BF}_3$.
3. The opinion is held that the cause of the described action of aprotic acids lies in their contribution to the heterolysis of the carbon to chlorine linkage, and that hydrogen exchange in these cases is related to the formation of carbonium ions.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE
WITH OLEFINS AND THEIR HYDROPOLYMERIZATION
UNDER THE ACTION OF CARBON MONOXIDE AND HYDROGEN
COMMUNICATION 29. CATALYTIC HYDROCONDENSATION
OF 2,4,4-TRIMETHYL-1-PENTENE

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An investigation of the catalytic hydrocondensation of trimethylethylene and tetramethylethylene with carbon monoxide showed that in contrast to normal α -olefins, these branched olefins react with difficulty and undergo only 5-10% of reaction; at the same time, 35-50% of the starting olefin is hydrogenated to isopentane and 2,3-dimethylbutane, respectively [1]. The only branched α -olefins whose hydrocondensation with CO has been investigated up to now are isobutylene [2,3] and isopropylethylene [4]. The two olefins behaved differently under these conditions. The isopropylethylene showed low activity and only 10% underwent the reaction. Twenty percent of it was hydrogenated to isopentane and approximately 4% was isomerized to trimethylethylene and partly to methylethylethylene. In contrast to isopropylethylene, isobutylene reacted readily and the total yield of liquid reaction products reached 50-60% on the starting isobutylene. In a mixture with hydrogen, isobutylene also underwent hydropolymerization to some extent in the absence of carbon monoxide; with the addition of carbon monoxide to the isobutylene-hydrogen mixtures there was a sharp increase in the yield of liquid reaction products.

In the present work we investigated the hydrocondensation with CO of the isobutylene dimer 2,4,4-trimethyl-1-pentene. As usual, we first studied the behavior of the olefin alone, then mixtures of it with hydrogen [5], and finally, the ternary mixtures $C_8H_{16}-H_2-CO$.

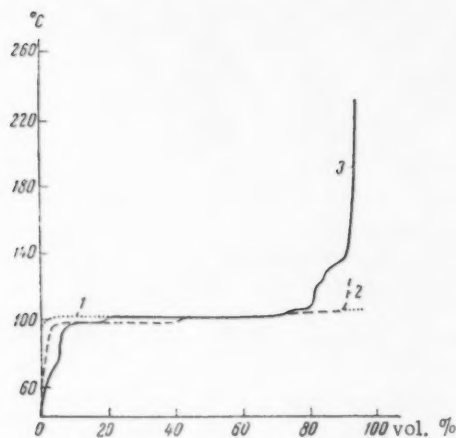
EXPERIMENTAL

The apparatus and experimental procedure were the same as those described previously [1-5]. The starting 2,4,4-trimethyl-1-pentene was synthesized by Butlerov's method [6] by polymerization of isobutylene with 63% sulfuric acid and the product was washed with 5% aqueous sodium carbonate solution and water, dried over baked potassium carbonate, boiled over sodium, and then fractionated on a column packed with triangular copper loops and with an efficiency of 40 theoretical plates. We collected a fraction with b.p. 101-102° (760 mm), which had n_D^{20} 1.4100; d_4^{20} 0.7158. Literature data for 2,4,4-trimethyl-1-pentene [7]: b.p. 101.36°; n_D^{20} 1.4086; d_4^{20} 0.7150. Two samples of Co-clay catalyst were used in the work and 30 ml portions of each were loaded into the glass reaction tube (10 mm in diameter) and regenerated with electrolytic hydrogen at 430° for 5 hr before each experiment. Each experiment lasted for 10-20 hr and was carried out at atmospheric pressure and 190°. The diisobutylene was fed into the reaction tube from an automatic burette. The liquid catalyzates from each experiment were dried and distilled on the column mentioned. The following fractions were collected: 1) boiling below 98°—hydrocracking and molecular disproportionation products boiling below isooctane and diisobutylene; 2) 98-101°, 101-102°, and 102-105°—2,4,4-trimethylpentenes and 2,2,4-trimethylpentane; 3) 105-125°—isomeric C_8 hydrocarbons, and, finally, 4) residue boiling above 125° and consisting of molecular disproportionation and hydrocondensation products boiling above diisobutylene and its isomers. The residues were distilled from a Wurtz flask for determination of the end of boiling. The experimental conditions and results obtained are given in Tables 1 and 2 and Fig. 1.

Experiments with C_8H_{16} . In experiment 1, which was carried out with 2,4,4-trimethyl-1-pentene in the absence of H_2 and CO, the catalyzate obtained boiled mainly over the range of 101-104°. The fraction with b.p. 98-101°, which represented 4.3% and had n_D^{20} 1.4064, indicated that the catalyzate contained small amounts (not more than

0.5%) of isooctane, which was apparently formed by hydrogenation of the starting olefin by hydrogen remaining on the catalyst surface after its reduction. The constants of the catalyzate (Table 2) show that it contained 2,4,4-trimethyl-2-pentene (~15%), which was formed by isomerization of the starting 2,4,4-trimethyl-1-pentene. A fraction of 2,4,

4-trimethyl-2-pentene with b.p. 104-105° and n_D^{20} 1.4170, representing 4% of the catalyzate obtained, was isolated directly. Neither cracking nor depolymerization of the diisobutylene to isobutylene was observed under the conditions of experiment 1.



Distillation curves of Catalyzates. 1) Experiment 1; 2) experiment 2; 3) experiment 8.

Experiments with $C_8H_{16}-H_2$ mixtures (experiments 2-6) were carried out with the amount of H_2 in the starting vapor-gas mixture varied over the wide range from 39 to 93%. The main reaction was hydrogenation of the starting 2,4,4-trimethyl-1-pentene to 2,2,4-trimethylpentane. The completeness of hydrogenation depended on the excess of H_2 with the result that the content of unsaturated hydrocarbons in the catalyzates varied from 0 to 57% (Table 2). However, the H_2 concentration in the starting vapor-gas mixture also affected the hydrocracking and molecular disproportionation. In actual fact, in experiment 2, where there was an excess of diisobutylene relative to the H_2 , the C_5-C_7 fraction (n_D^{20} 1.3854, d_4^{20} 0.6756) represented ~5% and did not contain C_5 hydrocarbons, as is shown by the temperature at which the catalyzate began to boil. No C_9 hydrocarbons and higher were formed. With an increase in the H_2 content to 64% and above, the yield of the C_5-C_7 fraction rose to 15.5% but did not exceed 19% with a H_2/C_8H_{16} ratio of 13.5 (experiment 6). This result is of independent

interest with respect to the mechanism of the destructive hydropolymerization of isobutylene we observed previously, as it shows [5] that the formation of 2,4,4-trimethylpentene is not an intermediate stage in this reaction. With an increase in the hydrogen concentration in the starting vapor-gas mixture (experiments 3-6) there was a fall

TABLE 1

No.	catalyst	expt.	Material passed				Starting vapor - gas mixture			Material collected			Composition of final gas		
			C_8H_{16} , ml	H_2 , liter n.p.t.	CO , liter n.p.t.	space velocity, hr^{-1}	comp., vol. %			liquid catalyzate, ml	final catalyzate, liter n.p.t.	vol. %	H	$C_n H_{2n+2}$	CO
							C_8H_{16}	H_2	CO						
1	1	96	0,0	0,0	45	100	0,0	0,0	96	0,2	—	—	—	—	—
1	2	83	7,5	0,0	74	60,8	39,2	0,0	83	1,5	94,3	5,7	0,0	0,0	0,0
1	3	89	22,2	0,0	116	36,0	64,0	0,0	89	12,3	87,8	12,2	0,0	0,0	0,0
2	4	80	16,3	0,0	92	41,6	58,4	0,0	79	5,9	64,0	34,8	0,0	0,0	0,0
2	5	39	47,2	0,0	109	10,3	89,7	0,0	35	45,6	89,5	10,2	0,0	0,0	0,0
2	6	51	100,8	0,0	172	6,9	93,1	0,0	49	95,0	99,4	0,0	0,0	0,0	0,0
1	7	91	11,8	2,2	89	48,5	43,5	8,0	91	7,5	92,0	0,0	7,0	7,0	7,0
1	8	88	9,4	1,5	77	53,6	40,0	6,4	88	3,6	90,8	2,0	7,2	7,2	7,2
1	9	53	7,4	0,9	53	47,0	46,5	5,5	53	1,5	93,0	0,4	0,2	0,2	0,2
2	10	88	18,6	3,0	103	37,7	56,3	9,0	83	8,3	69,6	24,0	6,0	6,0	6,0

in the temperature at which the catalyzates began to boil to 39.5°, indicating the formation of C_5 hydrocarbons, and a rise in the end of boiling of the catalyzates to 240-250°. The yield of C_9 hydrocarbons and higher did not exceed 5.5%. The residues containing these hydrocarbons had in experiment 4: n_D^{20} 1.4170 d_4^{20} 0.7317; and in experiment 6 n_D^{20} 1.4115, d_4^{20} 0.7304. The content of the isomeric C_8 hydrocarbons in the catalyzates was 4-7.7%.

Experiments with $C_8H_{16}-H_2-CO$ mixtures (experiments 7-10) were carried out with a CO content of the starting vapor-gas mixture of 5.5-9% and a H_2/C_8H_{16} ratio of 0.74-1.5. To estimate the effect of the addition of CO to $C_8H_{16}-H_2$ mixtures, we compared the results of experiments 2 and 8, which were carried out on the same catalyst with similar H_2/C_8H_{16} ratios (0.64 and 0.74) and space velocities (74 and 77 hr^{-1}). This comparison shows that the addi-

TABLE 2

Expt. no.	Properties of liquid catalyze					Comp. of liquid catalyzates, vol. %				
	begin. of boiling, °C	end of boiling, °C	d_4^{20}	n_D^{20}	bromine number	content of unsaturateds, %	C ₅ -H ₇ hydrocarbons, frac. < 98	diisobutylene + isooctane, frac. 98-105	isomeric C ₈ frac. 105-125	C ₉ and above, frac. > 125
1	98	105	0,7162	1,4110	—	—	0,0	100	—	0,0
2	60	127	0,7062	1,4019	81,7	57	4,6	85,9	7,7	0,0
3	45	241	0,6983	1,3952	19,7	14	15,4	70,6	4,7	5,0
4	45	253	0,6928	1,3936	18,1	12,5	16,0	66,2	7,7	5,5
5	39,5	249	0,6900	1,3915	2,2	1,5	18,7	70,0	4,6	4,4
6	40	—	0,6893	1,3928	0,0	0,0	17,5	73,0	4,0	4,0
7	60	232	0,7135	1,4079	122,5	87,0	9,1	81,7	3,1	3,2
8	48	234	0,7125	1,4059	87,0	61,5	8,2	74,0	4,3	10,0
9	46,5	242	0,7053	1,4019	72,0	51,3	14,0	66,6	7,2	10,8
10	43,5	242	0,7063	1,4039	113,6	82,5	11,1	71,4	7,1	5,4

tion of 6.4% of CO to the C₈H₁₆-H₂ mixture led to the appearance of 10% of C₉ and higher hydrocarbons in the catalyze (fraction with b.p. above 125°, n_D^{20} 1.4160, d_4^{20} 0.7389) with the end of boiling at 234°. The fraction of C₅-C₇ hydrocarbons increased from 4.6 to 8.2% and the beginning of boiling fell from 60 to 48°. A fall in the CO content to 5.5% (experiment 9) led to an increase in the yield of the fraction of hydrocondensation products (end of boiling 242°, n_D^{20} 1.4130, d_4^{20} 0.7324) to 10.8% and the fraction of C₅-C₇ hydrocarbons (n_D^{20} 1.3852, d_4^{20} 0.6772) to 14% in the catalyze. An increase in the CO concentration to 8-9% (experiments 7 and 10) completely stopped hydrocondensation and the yield of C₉ and higher hydrocarbons was the same as under analogous conditions with CO absent from the vapor-gas mixture, as is shown by a comparison of the results of experiments 4 and 10, which were carried out on the same catalyst sample under comparable conditions. It is noteworthy that the addition of CO and an increase in its content in the starting mixture reduced the hydrogenation of 2,4,4-trimethyl-1-pentene to 2,2,4-trimethylpentane, but did not have a strong effect on the hydrocracking. In actual fact, a comparison of experiments 2 and 8 and also 7 and 8 shows that the content of unsaturateds in the catalyze increased, while the yield of C₅-C₇ hydrocarbons changed little with the introduction of CO into the starting mixture and an increase in its concentration.

The results obtained show that in the absence of CO, 2,4,4-trimethyl-1-pentene changes little at 190° and atmospheric pressure on a Co—clay catalyst. There is partial migration of the double bond with isomerization to 2,4,4-trimethyl-2-pentene.

In mixtures with H₂, 2,4,4-trimethyl-1-pentene is hydrogenated to 2,2,4-trimethylpentane with the completeness of hydrogenation depending on the excess of H₂ in the starting vapor-gas mixture. At the same time there is hydrocracking and disproportionation as regards molecular weight [8]. When the olefin predominates in the starting mixture, these reactions occur to a slight extent: the content of C₅-C₇ hydrocarbons in the catalyze does not exceed 5% and the content of C₉ and higher, 5.5%. With excess H₂, the yield of C₅-C₇ hydrocarbons increases, but does not exceed 19%, even with the ratio H₂/C₈H₁₆=13.5. Skeletal isomerization products are obtained in a yield of not more than 7-8%. On addition of CO to the C₈H₁₆-H₂ starting mixture there is hydrocondensation of CO with diisobutylene to the extent of ~10% with a CO content of 5-6% in the starting vapor-gas mixture. At the same time there is 40-50% of hydrogenation of the starting olefin to isooctane. The yield of C₅-C₇ hydrocarbons is 10-14%. With an increase in the CO content to 8-9% in the starting mixture, hydrocondensation does not occur at all, while hydrogenation occurs only to the extent of 15-20%; the yield of liquid cracking products is 10%.

SUMMARY

1. When an equimolecular mixture of 2,4,4-trimethyl-1-pentene and hydrogen containing 5-6% of CO is passed over a Co—clay catalyst at 190° and atmospheric pressure there is ~10% of hydrocondensation of the starting olefin with carbon monoxide; in parallel, there is hydrogenation (main reaction), hydrocracking, molecular disproportionation, and isomerization.

2. An increase in the CO concentration to 8-9% stops hydrocondensation and reduces hydrogenation, but has little effect on hydrocracking.

3. In the absence of CO, hydrogenation of diisobutylene is the main reaction over a wide range of H₂/C₈H₁₆ ratios. Hydrocracking, molecular disproportionation, and isomerization occur to a small extent.

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BRIEF COMMUNICATIONS

VINYL ETHERS OF METHYL- AND DIMETHYLCYCLOPROPYLCARBINOLS

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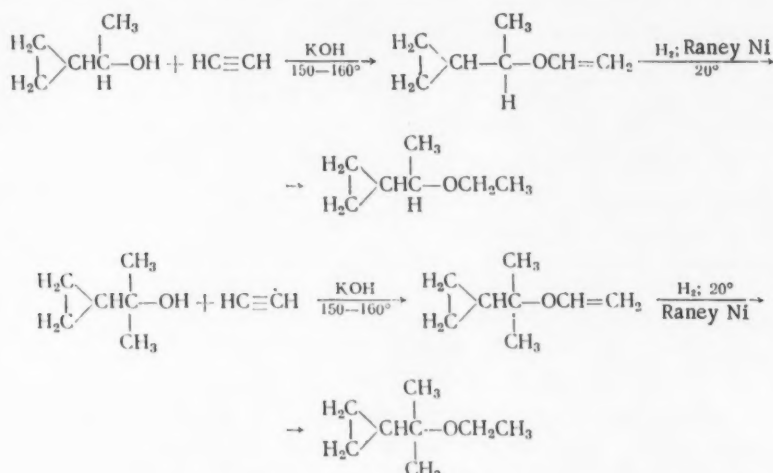
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pp. 2042-2043, November, 1960

Original article submitted April 1, 1960

Vinyl ethers containing a cyclopropyl group are of definite interest for studying the intereffect of the atoms forming the molecule and for investigating their polymerization.

We synthesized vinyl ethers of methyl- and dimethylcyclopropylcarbinols by the Favorskii-Shostakovskii method [1] and then hydrogenated them to the corresponding ethyl ethers:



The structures of the vinyl ethers obtained were confirmed by elementary analysis, Raman spectra, and also the spectra of their hydrogenation products. The presence in all the Raman spectra of intense bands in the regions of 1195-1200 and 3007-3010 cm^{-1} indicated that the cyclopropane ring was retained in all the compounds obtained. The above bands are absent from the Raman spectra of vinyl alkyl ethers [2]. The spectra of vinyl alkyl ethers contain a triplet of frequencies of valence vibrations of the double bond in the region of 1610, 1640, and 1650 cm^{-1} , which is explained by the presence of rotational isomerism and Fermi resonance in the ethers examined [2]. The spectrum of the vinyl ether of methylcyclopropylcarbinol also contained this triplet of frequencies. The spectrum of the vinyl ether of dimethylcyclopropylcarbinol contained only a doublet of frequencies, and this was probably connected with the absence of rotation isomers of this ether. The presence of double bond frequencies with vinyl ethers of the cyclopropane series and their absence from the spectra of the hydrogenation products indicated that the double bond of the vinyl ethers reacted completely.

EXPERIMENTAL

The starting methyl cyclopropyl ketone was obtained by the procedure we have described [3] and then reduced to methylcyclopropylcarbinol over a zinc catalyst [4].

Dimethylcyclopropylcarbinol. Over a period of 2 hr, 336 g of methyl cyclopropyl ketone was added with stirring and cooling in ice to the CH_3MgCl from 194 g of magnesium in 1.5 liter of ether. Stirring was continued for

4 hr at room temperature. After removal of the ether, the contents of the flask were then heated on a water bath at 60-70° for 10 hr, the distilled ether returned to the flask, and the complex decomposed with water and dilute acetic acid. The upper layer and ether extract from the lower layer were neutralized and dried with potassium carbonate. Distillation yielded 18 g of isopropenylcyclopropane with b.p. 70° (750 mm) and 334 g of dimethylcyclopropylcarbinol with b.p. 123° (755 mm); n_D^{20} 1.4338; d_4^{20} 0.8786; Found MR 29.67; Calculated MR 29.91; yield 83.5%. Literature data [5]: b.p. 123.4 (760 mm); n_D^{20} 1.4337; yield 68%.

Vinyl ether of methylcyclopropylcarbinol (1-vinyloxy-1-cyclopropylethane). A 127-g sample of methylcyclopropylcarbinol was heated to 150-160° with acetylene (17 atm) in the presence of 13 g of potassium hydroxide in a liter autoclave until the theoretical amount of acetylene had been absorbed. Acetylene was introduced twice. The normal treatment [2] yielded 122 g of the vinyl ether of methylcyclopropylcarbinol with b.p. 115 (746 mm); n_D^{20} 1.4284; d_4^{20} 0.8392; found MR 34.41; Calculated MR 34.42; yield 73.8%. Found: C 74.85; 74.90; H 10.70; 10.74% C₇H₁₂O. Calculated: C 74.95; H 10.76%.

Raman spectrum, $\Delta\nu$, cm⁻¹: 170 (1); 240 (v. broad); 309 (v. broad); 315 (v. broad); 366 (v. broad doublet); 384 (0); 430 (1 broad); 455 (0); 482 (1 broad); 502 (1 broad); 513 (1 broad); 548 (1 broad); 768 (3 broad); 794 (0); 828 (6 broad); 852 (5 broad); 898 (1); 914 (3); 932 (4 broad); 954 (0); 977 (2 broad); 1020 (0); 1067 (0); 1085 (0); 1110 (0, broad); 1170 (1); 1200 (6 broad); 1222 (2 broad); 1310 (6); 1337 (3 broad); 1396 (2 broad); 1433 (3 broad); 1453 (2 broad); 1467 (3 broad); 1500 (1 broad); 1610 (1); 1635 (4 broad); 1652 (0); 2870 (4 broad); 2935 (5 broad); 2970 (3 broad); 3010 (10 broad); 3075 (5 broad).

Hydrogenation of the vinyl ether of methylcyclopropylcarbinol yielded the ethyl ether of methylcyclopropylcarbinol with b.p. 111° (741 mm); n_D^{20} 1.4065; d_4^{20} 0.8121; found MR 34.57; Calculated MR 34.89.

Raman spectrum, $\Delta\nu$, cm⁻¹: 368 (2 broad); 510 (1 broad); 758 (3 broad); 792 (0); 823 (3 broad); 852 (5); 892 (0); 910 (2 broad); 928 (3 broad); 960 (0); 1095 (1 broad); 1195 (7); 1225 (2); 1268 (v. broad); 1383 (1); 1430 (1); 1450 (3 broad); 1462 (3 broad); 2870 (5 broad); 2935 (7 broad); 2972 (5); 3007 (7); 3075 (4 broad).

Vinyl ether of dimethylcyclopropylcarbinol (2-vinyloxy-2-cyclopropylpropane). Under the conditions given above, 150 g of dimethylcyclopropylcarbinol was vinylated in the presence of 30 g of potassium hydroxide. Acetylene was introduced three times and its absorption was a factor of three slower than in the case of methylcyclopropylcarbinol. Analogous treatment [2] yielded 80 g of the starting dimethylcyclopropylcarbinol and 47.3 g of the vinyl ether of dimethylcyclopropylcarbinol with b.p. 133.8° (761 mm); n_D^{20} 1.4380; d_4^{20} 0.8497; found d_4^{20} 38.89; Calculated: MR 39.06; yield 15%, calculated on the dimethylcyclopropylcarbinol taken for the reaction. Found: C 76.33; 76.23; H 11.34; 11.21%. C₈H₁₄O. Calculated: C 76.13; H 11.18%.

Raman spectrum, $\Delta\nu$, cm⁻¹: 306 (1 broad); 368 (3 broad); 418 (1 broad); 487 (2 broad); 506 (3); 540 (2 broad); 700 (v. broad); 760 (3 broad); 822 (5 broad); 850 (8); 890 (0); 910 (3 broad); 928 (4 broad); 950 (v. broad); 1020 (v. broad); 1046 (v. broad); 1093 (2 broad); 1110 (2 broad); 1163 (1 broad); 1195 (10); 1208 (5 broad); 1242 (3 broad); 1272 (1); 1303 (5 broad); 1332 (2 broad); 1392 (3 broad); 1430 (3); 1447 (4 broad); 1464 (4 broad); 1630 (8 broad); 1652 (0); 2870 (5 broad); 2930 (6); 2970 (7); 3008 (9); 3075 (5 broad).

Hydrogenation of the vinyl ether of dimethylcyclopropylcarbinol, which proceeded at half the rate of the hydrogenation of the vinyl ether of methylcyclopropylcarbinol, yielded the ethyl ether of dimethylcyclopropylcarbinol with b.p. 126.8° (761 mm); n_D^{20} 1.4160; d_4^{20} 0.8239; found MR 39.65; calculated MR 39.54.

Raman spectrum, $\Delta\nu$, cm⁻¹: 345 (3 broad); 365 (2 broad); 390 (3 broad); 430 (6); 476 (2); 505 (1 broad); 530 (1); 558 (3); 630 (8); 705 (7); 762 (0); 787 (3 broad); 823 (9); 832 (7); 893 (5 broad); 910 (5 broad); 922 (5 broad); 945 (4 broad); 998 (1); 1022 (1); 1052 (1); 1055 (1 broad); 1078 (4 broad); 1115 (3 broad); 1163 (1 broad farad); 1200 (10); 1215 (6 broad); 1238 (2); 1275 (3); 1310 (1); 1360 (2 broad); 1390 (2 broad); 1442 (3 broad); 1462 (5); 1485 (1); 2870 (5); 2905 (3 broad); 2930 (10); 2945 (8); 2975 (10); 3010 (10); 3080 (6 broad).

The authors would like to thank G. K. Gaivoronskaya, who plotted the spectra on an ISP-51 spectrograph.

SUMMARY

1. The vinyl ethers of methyl- and dimethylcyclopropylcarbinol were synthesized.
2. Due to high steric hindrance, the vinylation of dimethylcyclopropylcarbinol and also the hydrogenation of its vinyl ether were much slower than in the case of methylcyclopropylcarbinol.

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INVESTIGATION OF THE EFFECT OF CHO GROUPS
IN THE CELLULOSE MOLECULE ON THE STABILITY
OF THE ACETAL BOND IN AN ACID MEDIUM
USING MODEL COMPOUNDS

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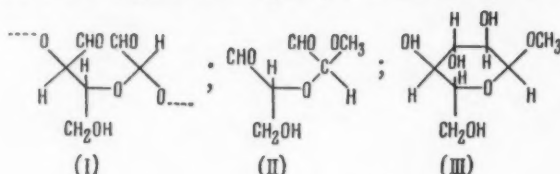
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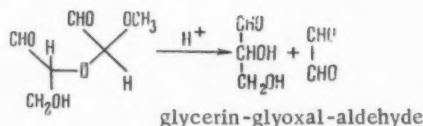
In our previous work it was reported that fragments of type (I) (i.e., glucose residues oxidized to CHO groups at C₂ and C₃) appear in the cellulose molecule on treatment with a number of oxidizing agents [1] and there is also the possibility that they may be present in samples of so-called native cellulose [2]. The few available data on the behavior of oxycelluloses containing fragments of type (I) indicate that they are quite stable to dilute acids at room temperature [3] and less stable to these acids at higher temperatures, but in any case they are less stable than celluloses without fragments of type (I) [4]. One explanation for this behavior of the oxycelluloses considered above may be weakening of the glucosidic bond in the oxycelluloses under the influence of the CHO groups at C₂ and C₃. The investigation of this problem by comparative hydrolysis of oxidized and unoxidized celluloses themselves is complicated by the presence of a supermolecular structure, making it necessary to carry out the hydrolysis in a heterogeneous medium. The investigation of this problem with model compounds eliminates the question of the effect of the supermolecular structure.

In the present communication we present comparative results obtained by studying the rate of hydrolysis of a model of oxidized cellulose with fragments of type (I), and a model of unoxidized cellulose by aqueous hydrochloric acid. The results obtained show that compound (II) is hydrolyzed more rapidly than compound (III).



EXPERIMENTAL

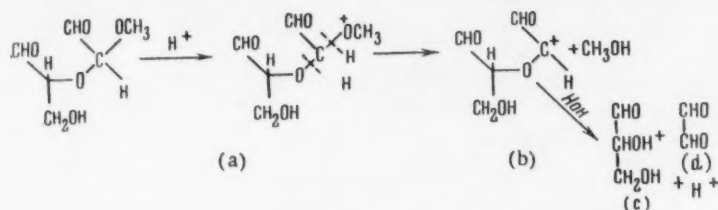
D'-Methoxy-D-hydroxymethylglycolaldehyde (II) was prepared as a model of oxidized cellulose containing fragments of type (I), and α -methylglucoside (III) was used as a model of unoxidized cellulose. Compounds (II) and (III) were hydrolyzed in 1 N aqueous HCl at 60 and 80° in a thermostat controlled with an accuracy of $\pm 0.5^\circ$. The degree of hydrolysis of α -methylglucoside was found by iodometric determination [5] of the number of aldehyde groups formed by hydrolytic cleavage. Hydrolysis of compound (II) proceeded in accordance with scheme I:



In this case, the degree of hydrolysis was determined from the increase in the number of aldehyde groups as a result of the formation of glyceraldehyde and glyoxal. The aldehyde groups were also determined iodometrically in an alkaline medium [6].

The data obtained show that D'-methoxy-D-hydroxymethyldiglycolaldehyde is hydrolyzed 14 times as fast as α -methylglucoside by 1 N HCl at 60° and eight times as fast at 80° (Tables 1 and 2).

The mechanism of the acid hydrolysis of compound (II) may be represented as follows:



According to this scheme, the limiting stage [7] is the hydrolytic decomposition of the momentarily formed oxonium ion (a) with the formation of carbonium ion (b), which rapidly adds a water molecule to give the final hydrolysis products (c) and (d).

TABLE 1. Hydrolysis of D'-Methoxy-D-hydroxymethyldiglycolaldehyde by 1 N HCl at 60°.

Hydrolysis time, hr	Deg. of hydrolysis, %	$K_{II}^{*} 10^{-5}$ sec ⁻¹	$\frac{K_{II}}{K_{III}}$	Remarks
2	27,39	4,45	14	$K_{III}=0,28 \cdot 10^{-5}$ sec ⁻¹
3	37,96	4,44		
4	42,25	3,91		
6	52,40	3,43		
Average		4,05**		

TABLE 2. Hydrolysis of D'-Methoxy-D-hydroxymethyldiglycolaldehyde by 1 N HCl at 80°.

Hydrolysis time, hr	Deg. of hydrolysis, %	$K_{II}^{*} 10^{-4}$ sec ⁻¹	$\frac{K_{II}}{K_{III}}$	Remarks
10	15,64	2,84	8	$K_{III}=0,24 \cdot 10^{-4}$ sec ⁻¹
15	18,55	2,28		
30	28,15	1,84		
60	47,75	1,87		
120	52,76	1,04		
Average		1,97**		

Since the acetal bond in (II) is hydrolyzed more rapidly than that in (III), (see Tables 1 and 2), the introduction of a CHO group into the α -position relative to this bond creates more favorable conditions for hydrolytic cleavage of the oxonium ion (a) formed. From our previous work [5] it follows that COOH groups have a similar effect, and according to work of other authors [8], this also applies to CH₂OH groups at C₂ and C₄ of corresponding derivatives of α -methylglucoside. Since cleavage of the C-OCH₃ bond must give the carbonium ion (b), according to the vicinal effect, the greater the I-effect of the left-hand side of the molecule, the more stable will be the acetal bond C-OCH₃. Consequently, the unoxidized unit of α -methylglucoside (III) has a greater I-effect than the oxidized pyran unit with COOH, CHO, and CH₂OH groups at C₂ and C₄.

The appearance of open pyran units with COOH, CHO, and CH₂OH groups at C₂ and C₃ in the cellulose molecule may be one of the causes of the existence in it of weaker places with respect to acid hydrolysis.

SUMMARY

1. Comparison of the hydrolysis rates of D'-methoxy-D-hydroxymethyldiglycolaldehyde and α -methylglucoside showed that a CHO group in the α -position relative to an acetal bond lowers the stability of the latter in an acid medium.

2. The formation of CHO groups at C₂ and C₃ in an oxidized unit of a cellulose molecule must lead to weakening of the acetal bond in it in an acid medium.

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*K represents the hydrolysis rate constants of the compounds examined.

**The decrease in the hydrolysis rate constant is connected with a change in the hydrolysis products, in particular, glyoxal.

HYDROGENOLYSIS OF C₇ ALKANES IN THE PRESENCE OF NICKEL-ALUMINA CATALYST UNDER A PRESSURE OF HYDROGEN

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A number of investigations have been devoted to the catalytic hydrogenolysis of alkanes [1-3]. In order to obtain highly branched hydrocarbons, for example, tryptane, Haensel and Ipatieff [4] investigated the selective demethylation of alkanes with quaternary and ternary carbon atoms in the presence of nickel on Kieselguhr under a pressure of hydrogen. In an investigation of the structure of high-molecular alkanes, Koch [5] demethylated them on a cobalt catalyst, while Tilicheev and Polyakova used nickel [6]. One of us [7] showed that the demethylation of n-alkanes proceeds readily on a skeletal Ni-Al catalyst in the vapor phase with hydrogen at normal pressure. We recently determined the optimal conditions for the demethylation of methylcyclohexane [8] and the hydrogenolysis of the side chain of other monoalkyl-cyclohexanes [9] in the presence of a nickel-alumina catalyst at a high hydrogen pressure.

To determine the degree of selectivity of the catalyst and the effect of the structure of some C₇ alkanes on the nature and extent of their hydrogenolysis, in the present work we used n-heptane, 3-methylhexane, 2,4-dimethylpentane, and 2,2-dimethylpentane for investigation. The first two of these hydrocarbons are present together with methylcyclohexane in the heptane - methylcyclohexane fraction of ligoins from primary distillation, while the next two may be present in the benzene-cyclohexane fraction of ligoins.

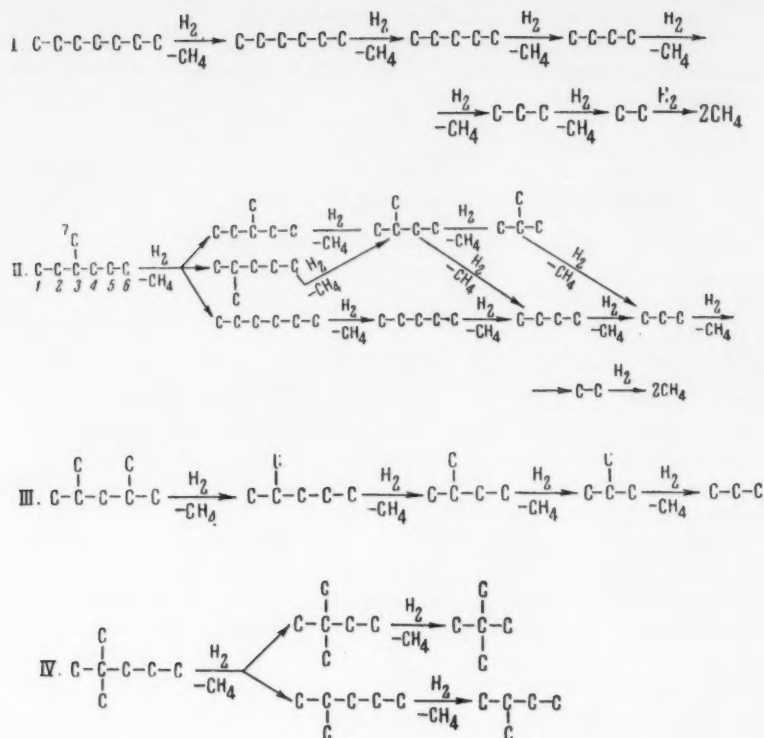
The starting hydrocarbons had the following properties:

	b.p. (760 mm)	n_D^{20}	d_4^{20}
n-Heptane	98.4	1.3875	0.6840
3-Methylhexane	91.6	1.3884	0.6875
2,4-Dimethylpentane	80.3	1.3815	0.6730
2,2-Dimethylpentane	79.4	1.3820	0.6742

Their hydrogenolysis was carried out in a flow system at 360° under a hydrogen pressure of 20 atm with a molar ratio of hydrogen to hydrocarbon of 4 : 1 and a space velocity of 0.2 hr⁻¹. The composition of the liquid catalyzate was determined by gas-liquid chromatography; the emergent gases were analyzed on a chromatographic gas analyzer. The data obtained are given in the table.

The results obtained show that the alkanes studied underwent only hydrogenolysis in contact with 10% Ni-Al₂O₃ under the conditions adopted; there was no isomerization of the alkanes. Under the same conditions, methylcyclohexane and cyclohexane were isomerized with ring contraction to the corresponding pentamethylene hydrocarbons. However, it should be noted that the demethylation of 2,4-dimethylpentane proceeded with somewhat greater difficulty than the demethylation of the other alkanes. The catalyzate from 2,2-dimethylpentane contained no hydrocarbons with less than five carbon atoms if methane is ignored. These results agree with the conclusion of Haensel and Ipatieff on the great ease of hydrogenolysis of a methyl group attached to a secondary carbon atom in comparison with the hydrogenolysis of a methyl group attached to a tertiary, and especially, a quaternary carbon atom.

The composition of the gases and liquid catalyzates obtained, apparently shows that the hydrogenolysis of the alkanes we investigated proceeds largely by successive demethylations [7]. On the basis of the results obtained we propose the following schemes for the hydrogenolysis of C₇ alkanes of various structures:



TABLE' Composition of Liquid and Gaseous Catalysts

Starting hydrocarbons		n-Heptane	3-Methylpentane	2,4-Dimethylpentane	2,2-Dimethylpentane
Liquid catalyzate yield, %		80,2	81,0	84,0	82,5
Composition of liquid catalyzates	n-Heptane	78,5	—	—	—
	3-Methylhexane	—	78,1	—	—
	2,4-Dimethylpentane	—	—	89,2	—
	2,2-Dimethylpentane	—	—	—	78,5
	n-Hexane	14,7	1,0	—	—
	2-Methylpentane	—	6,2	9,1	2,1
	3-Methylpentane	—	9,0	—	—
	2,2-Dimethylbutane	—	—	—	17,3
	n-Pentane	5,0	0,9	traces	—
	2-Methylbutane	—	3,7	1,1	0,6
	2,2-Dimethylpropane	—	—	—	1,5
Composition of emergent gases	n-Butane	1,4	0,5	traces	—
	2-Methylpropane	—	0,4	0,6	—
	Propane	0,4	0,2	traces	—
	H ₂	84,8	89,6	96,6	93,2
	CH ₄	14,0	10,2	3,3	6,8
	C ₂ H ₆	~0,1	~0,2	—	—
	C ₃ H ₈	~0,1	—	~0,1	—

It is interesting to note that in the molecule of 3-methylhexane, which has two methyl groups attached to a secondary carbon atom, the 5-6 C-C bond undergoes hydrogenolysis more readily than the 1-2 bond, as is shown by a comparison of the yields of 3-methylpentane and 2-methylpentane. Thus, under the conditions we adopted, the tertiary carbon atom in the molecules of 3-methylhexane not only has a passivating effect on the hydrogenolysis of the methyl group attached to it, but also on the relative ease of hydrogenolysis of adjacent C-C bonds. The hydro-

genolysis of C—C bonds that are more remote from the tertiary carbon atom proceeds at a higher rate. This rule of preferential hydrogenolysis of C—C bonds most remote from a carbon atom bearing substituents is expressed even more definitely in the hydrogenolysis of 2,2-dimethylpentane, whose molecule contains a quaternary carbon atom.

SUMMARY

1. The hydrogenolysis of n-heptane, 3-methylhexane, 2,4-dimethylpentane, and 2,2-dimethylpentane on a 10% Ni—Al₂O₃ catalyst at 360° and a hydrogen pressure of 20 atm was investigated.

2. A relation was found between the position of preferential hydrogenolysis of C—C bonds in the molecules of these alkanes and their skeletal structure. In molecules of branched alkanes, C—C bonds at the greatest distance from the tertiary and quaternary carbon atoms underwent hydrogenolysis preferentially.

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CYCLOALKENYLATION OF PHENOL WITH 1,3-CYCLOHEXADIENE

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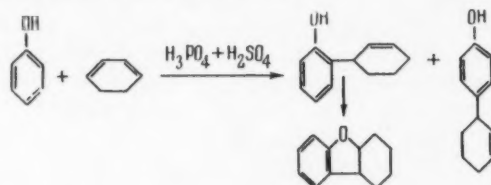
Translated from *Izvestiya Akademii Nauk, Otdelenie Khimicheskikh Nauk*, No.11,

pp. 2048-2050, November, 1960

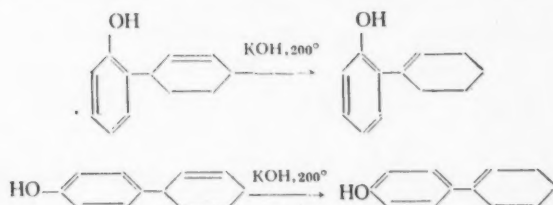
Original article submitted April 19, 1960

No investigations on the cycloalkenylation of phenols with cyclohexadiene have been published up to now. The literature contains only formally analogous work on the alkenylation of phenol [1] and isomeric cresols [2,3] with cyclopentadiene in the presence of phosphoric acid.

In the present work we studied the cycloalkenylation of phenol with 1,3-cyclohexadiene in the presence of phosphoric acid and a mixture of phosphoric and sulfuric acids in a ratio of 6 : 1. With the use of this mixture (with a weight of it equal to 70% of the weight of the reagents) and a reaction temperature of 20-30°, it was possible to reach a total yield of cycloalkenylation products of up to 80%. From the cycloalkenylation products we isolated o- and p-(cyclohexen-2-yl)phenols in 67% yield, 2,3-cyclohexano-2,3-dihydrobenzofuran (5%), and also, apparently, di-(cyclohexen-2-yl)phenols (8%), whose structure was not determined.



2,3-Cyclohexano-2,3-dihydrobenzofuran was formed as a result of cyclization of o-(cyclohexen-2-yl)phenol during the reaction, as was confirmed by cyclization of o-(cyclohexen-2-yl)phenol with hydrobromic acid. The o- and p-(cyclohexen-2-yl)phenols were isomerized to the corresponding (cyclohexen-1-yl)phenols by potassium hydroxide at 200°:



EXPERIMENTAL

1,3-Cyclohexadiene was synthesized by the method described by Domnin [2] in 68% of theoretical yield: b.p. 79-81° (760 mm); n_D^{20} 0.8414. Literature data [4]: b.p. 79-80°; n_D^{15} 1.4740 and d_4^{15} 0.8400.

Synthesis of o- and p-(cyclohexen-2-yl)phenols. Into a flask fitted with a mechanical stirrer, bulb condenser, thermometer, and gas inlet tube were placed 72.8 g (0.75 mole) of phenol in 90 ml of absolute toluene, 86 g of phosphoric acid (sp.g. 1.69), and 13 g of sulfuric acid (sp.g. 1.84), and a stream of nitrogen was passed while 62 g (0.75 mole) of 1,3-cyclohexadiene was introduced over a period of 4 hr with the temperature of the reaction mixture not allowed to rise above 30°. The reaction mixture was stirred for a further 8 hr at room temperature and then the acid layer separated and the toluene layer treated with 10% sodium hydroxide solution. The alkaline extract was treated with acid and the liberated phenols were dried and vacuum distilled to give, in addition to the starting phenol, two substances with the following properties:

1) 50 g of o-(cyclohexen-2-yl)phenol with b.p. 119-121° (3 mm); n_D^{20} 1.5670; d_4^{20} 1.0735; found MR 52.97. $C_{12}H_{14}O_4E_4$. Calculated MR 52.88. Its yield was 39% of theoretical. The melting point of the phenoxy derivative was 129-130°. Found: C 72.36; 72.16; H 6.95; 7.04%. $C_{14}H_{16}O_3$. Calculated: C 72.38; H 6.93%. The methyl ether had b.p. 144-146° (22 mm), n_D^{20} 1.5522; d_4^{20} 1.0354; found MR 58.49. $C_{13}H_{16}O_4E_4$. Calculated MR 58.71. Oxidation of the methyl ether with permanganate gave o-methoxybenzoic acid with m.p. 99-100°. Literature data [5] m.p. 100-101°.

2) 16 g of p-(cyclohexen-2-yl)phenol with b.p. 139-141° (3 mm); m.p. 72.8-73°; yield 28% of theoretical. Melting point of phenoxy derivative, 109-110°. Found: C 72.42; 72.55; H 7.04; 7.11%. $C_{14}H_{16}O_3$. Calculated: C 72.38; H 6.93%. The methyl ether had b.p. 150-151° (22 mm); n_D^{20} 1.5475 and d_4^{20} 1.0275; found MR 58.49; calculated MR 58.71. Oxidation of this ether gave p-methoxybenzoic acid with m.p. 184.2-184.5°.

According to literature data, this acid has m.p. 184.2-184.4° [5]. From the neutral part of the catalyze we isolated 5 g of 2,3-cyclohexano-2,3-dihydrobenzofuran (yield -5% of theoretical) with b.p. 110-112° (3 mm); n_D^{20} 1.5538 and d_4^{20} 1.0784; found MR 51.45. $C_{12}H_{14}O_3E_3$. Calculated 51.25.

To confirm the structure of the substance isolated, we cyclized o-(cyclohexen-2-yl)phenol with hydrobromic acid. For this purpose, 20 ml of glacial acetic acid and 10 ml of 48% hydrobromic acid were added to 10 g of o-(cyclohexen-2-yl)phenol and the reaction mixture was heated for 4 hr on a water bath. The reaction mixture was then extracted with ether, the ether extract washed with alkali and then water and dried, and the residue after removal of the ether vacuum distilled. We obtained 3.6 g of a substance with b.p. 111-112° (3 mm); n_D^{20} 1.5532 and d_4^{20} 1.0970. The yield of the 2,3-cyclohexano-2,3-dihydrobenzofuran obtained in this way was 36%.

Isomerization of (cyclohexen-2-yl)phenols to (cyclohexen-1-yl)phenols. For the isomerization, 13 g of o-(cyclohexen-2-yl)phenol was placed in a three-necked flask fitted with a stirrer, thermometer, and gas inlet tube, and heated to 200° in a stream of nitrogen, and then 14.5 g of powdered potassium hydroxide added to it gradually. Heating was continued for 4 hr. The reaction mixture was then acidified and the liberated phenol extracted with ether. The extract was dried, the ether removed, and the residue vacuum distilled. In addition to unchanged o-(cyclohexen-2-yl)phenol, we isolated 5 g (38%) of o-(cyclohexen-1-yl)phenol with b.p. 139-145° (7 mm) and m.p. 89-91°; the yield was 38%. The melting point of the phenoxy derivative was 137.8-138.5°. The sodium salt of the phenoxy derivative was insoluble in water, while that of o-(cyclohexen-2-yl)phenol was readily soluble in water.

Isomerization of p-(cyclohexen-2-yl)phenol under analogous conditions gave a 40% yield of p-(cyclohexen-1-yl)phenol with b.p. 148-149° (4 mm) and m.p. 109-110°. The melting point of its phenoxy derivative was 146-147°.

SUMMARY

1. The cycloalkenylation of phenol with 1,3-cyclohexadiene in the presence of a mixture of phosphoric and sulfuric acids was studied.
2. The reaction products were o-(cyclohexen-2-yl)phenol in 39% yield and p-(cyclohexen-2-yl)phenol in 28% of theoretical yield.
3. Isomerization of o- and p-(cyclohexen-2-yl)phenols in the presence of potassium hydroxide gave the corresponding (cyclohexen-1-yl)phenols.
4. The cyclization product of o-(cyclohexen-2-yl)phenol was 2,3-cyclohexano-2,3-dihydrobenzofuran.

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ACIDITY FUNCTIONS OF SOLUTIONS OF PROPYLENE IN AQUEOUS SULFURIC ACID

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In studying the relation of the rate of acid-catalyzed reactions to the acidity of the medium, it is necessary to consider the effect of the reagents on the value of the latter. However, only a few papers [1-5] have been devoted to the effect of organic compounds on the acidity function of aqueous solutions of strong acids. In the case of acid-catalyzed conversions of propylene, at sufficiently high concentrations of the latter in solution, it is also necessary to consider its effect on the acidity function of the medium.

In the present work we investigated the change in the acidity function of 66.83% H_2SO_4 on solution of propylene in it, which, as we showed previously [6], is accompanied by the simultaneous formation of an alkyl acid and alcohol. An indicator method was used for the measurements. As the indicator, we used 2,4-dinitroaniline, whose unprotonized form has an absorption spectrum with a maximum at $\lambda = 350 m\mu$. The absorption coefficient of the protonized form is practically zero in this region. The values of the acidity function were calculated from a known formula [7]:

$$H_0 = pK_B + \lg \frac{c_B}{c_{BH^+}} = pK_B + \lg \frac{c_B}{c_0 - c_B},$$

where $pK_B = -\log K_B$, K_B is the reciprocal basicity constant of the indicator B, c_0 is the total concentration of the indicator in the starting acid, and c_B and c_{BH^+} are the concentrations of the unprotonized and protonized forms of the indicator, respectively.

The change in acidity function with a change in the medium composition is expressed by the formula

$$\Delta H_0 = H_{0i} - H_0 = \lg \frac{c_{B_0}(c_0 - c_{B_i})}{c_{B_i}(c_0 - c_{B_0})}, \quad (1)$$

where the subscripts 0 and i refer to the starting acid and solutions containing various amounts of propylene. If the Lambert-Beer law holds for the system studied, then $c_B = D_B / \epsilon$, where D_B is the optical density of the solution and ϵ is the absorption coefficient of the indicator B. The total concentration of the indicator in the solution $c_0 = m/V_i$ where m is the amount of indicator and V_i is the solution volume. Then expression (1) acquires the following form:

$$\Delta H_0 = \lg \frac{D_{B_s} \left(\frac{m}{V_i} - \frac{D_{B_i}}{\epsilon} \right)}{D_{B_i} \left(\frac{m}{V_0} - \frac{D_{B_s}}{\epsilon} \right)} = \lg \frac{D_{B_s} \left(D_0 \frac{V_0}{V_i} - D_{B_i} \right)}{D_{B_i} \left(D_0 \frac{V_0}{V_0} - D_{B_s} \right)} = \lg \frac{D_{B_s} (D_{0\rho} - D_{B_i})}{D_{B_i} (D_0 - D_{B_s})}, \quad (2)$$

where $\rho = V_0/V_i = d_i/d_0$; d is the specific gravity of the solution, and D_0 is the optical density of a solution in which the whole of the indicator is in the unprotonized form.

The optical density was measured on an SF-4 quartz spectrophotometer in completely fused quartz cells, 5 cc in capacity and 1.5 cm in length, placed in thermostatted cell-holders. Propylene was introduced into the acid directly in the cell, which was then used for measuring the optical density of the solution. The cell, filled with acid and indicator and connected to a gas burette with a flexible hose, was placed in a thermostat and shaken vigorously with a frequency of ~500 oscillations per min. The amount of propylene absorbed was determined from the decrease in the amount of gas in the burette. The comparison cell contained 66.83% H_2SO_4 . The difference between the optical density of sulfuric acid containing propylene and the starting acid was allowed for on the basis of special experiments.

The optical densities D required for the calculation of ΔH_0 were measured at the absorption maximum of 2,4-dinitroaniline at $\lambda = 350 \text{ m}\mu$.

The specific gravities of the solutions investigated were measured with a specially constructed pycnometer of the Ostwald type with a capacity of 1 cc. The pycnometer was filled by a method which made it possible to transfer the solution directly from the cell under pressure without loss of gas, as occurs with normal suction. All measurements were made at 50° . Figure 1 shows the absorption spectra of solutions of 2,4-dinitroaniline in 66.83% H_2SO_4 containing various amounts of dissolved propylene. As Fig. 1 shows, the optical density of the solutions increased with an increase in the concentration of propylene, which indicates an increase in the concentration of unionized indicator molecules. The table gives the optical densities of the solutions investigated, their specific gravities, and also the changes in the acidity functions calculated from these data.

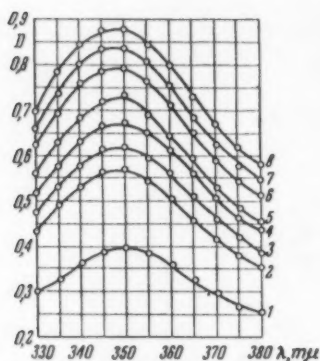


Fig. 1. Absorption spectrum of 2,4-dinitroaniline in solutions of C_3H_6 in 66.83% H_2SO_4 of various compositions. Concentrations of C_3H_6 in moles/liter of solution: 1) 0; 2) 2.22; 3) 2.85; 4) 3.59; 5) 4.33; 6) 5.88; 7) 7.36; 8) 8.27.

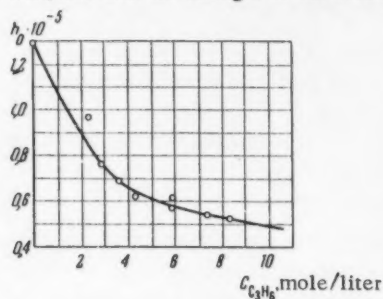


Fig. 2. Relation of medium acidity to the concentration of absorbed propylene.

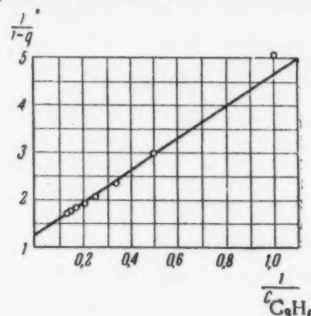


Fig. 3. Graph for calculation of the parameters a and b in equation (3).

Figure 2 shows the relation of the acidity of the medium to the concentration of absorbed propylene. Between the acidity of the starting solution h_0 and the acidity of a solution containing $c_{\text{C}_3\text{H}_6}$ mole/liter of propylene, h_{0i} , there is an empirical relation of the following form:

$$h_{0i} = h_0 \left(1 - \frac{ac_{\text{C}_3\text{H}_6}}{1 + bc_{\text{C}_3\text{H}_6}} \right).$$

The parameters a and b in equation (3) were calculated from a graph in the coordinates $\frac{1}{1-q} - \frac{1}{c_{\text{C}_3\text{H}_6}}$ (Fig. 3), where $q = \frac{h_{0i}}{h_0}$; $a = 0.3$, $b = 0.4$.

TABLE Change in Acidity Function of 66.83% H_2SO_4 on Absorption of Propylene.

$c_{\text{C}_3\text{H}_6}$	d , g/cm ³	D_{B_i}	ΔH_0	$-H_{0i}$	$h_{0i} \cdot 10^{-5}$
0	1,542	0,38	0	5,11	1,29
2,22	1,506	0,55	0,18	4,93	0,96
2,85	1,493	0,60	0,23	4,88	0,76
3,59	1,478	0,66	0,27	4,84	0,69
4,33	1,463	0,72	0,32	4,79	0,62
5,88	1,430	0,78	0,35	4,76	0,57
5,93	1,428	0,74	0,32	4,79	0,61
7,36	1,398	0,82	0,37	4,74	0,54
8,27	1,374	0,86	0,39	4,72	0,52

On solution in 66.83% H_2SO_4 , the propylene was 75% converted into isopropanol [6], whose appearance was mainly responsible for the fall in the acidity function. Although the alcohol is a weaker base than water [8-10], its role in the aqueous solution of the acid apparently consisted of disrupting the large aggregates of water molecules formed through hydrogen bonds [8,9]. As a result of addition of the alcohol, there was an increase in the number of free water molecules, which are stronger proton acceptors than molecules present in aggregates.

SUMMARY

1. When propylene is absorbed by aqueous sulfuric acid, there is a fall in the acidity function of the medium. The acidity change is well described by an empirical formula.

2. The densities of solutions of propylene in 66.83% H_2SO_4 at 50° were measured.

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SULFUR - CONTAINING LACTAMS AND THEIR POLYMERS

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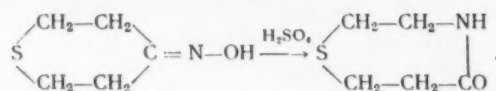
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No.11,

pp. 2053-2054, November, 1960

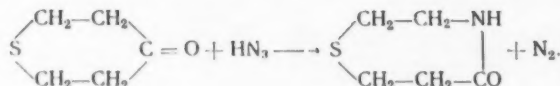
Original article submitted, April 18, 1960

The greatly increased value of synthetic fibers has drawn the attention of research workers to the study of various analogues of the polyamide resins; in particular, the preparation of sulfur containing polyamides and their polymers has been reported [1]. In the present paper are described previously unknown lactams and their polymers which contain in the carbon chain sulfur atoms of the sulfide and sulfone types.

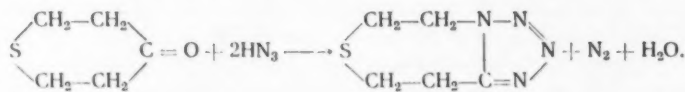
The lactam of β -aminoethylthioxy- ω -propionic acid was obtained by the Beckmann rearrangement - by heating tetrahydro- γ -thiopyrone oxime with concentrated sulfuric acid:



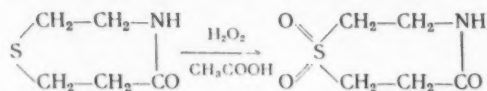
The same lactam was successfully prepared by the Schmidt reaction - by treating tetrahydro- γ -thiopyrone with hydrazoic acid:



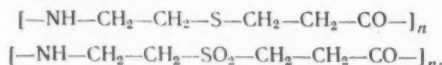
If an excess of hydrazoic acid was used in the last example, then the basic reaction product was 1,2-tetrazole- β, β' -diethylsulfide:



On oxidizing the lactam of β -aminoethoxy- ω -propionic acid with hydrogen peroxide in glacial acetic acid the lactam of β -aminoethanesulfo- ω -propionic acid is obtained quantitatively:



Both lactams are colorless crystalline substances which are soluble in water and most organic solvents. On heating the lactams in the presence of various additives (e.g. water, dry sodium hydroxide, metallic sodium) polymerization takes place to form the respective polyamides:



The polyamides are transparent fibers or films which are insoluble in water and most organic solvents. They soften at temperatures $\sim 200^\circ$.

EXPERIMENTAL

Rearrangement of tetrahydro- γ -thiopyrone oxime*. A mixture of 18.4 g concentrated sulfuric acid and 1.1 g tetrahydro- γ -thiopyrone oxime was heated to boiling, and sulfur dioxide began to separate. The mixture was then cooled to room temperature and poured into ice. After neutralizing (to litmus) by passing in gaseous ammonia, the

*Tetrahydro- γ -thiopyrone oxime was prepared by treating tetrahydro- γ -thiopyrone with hydroxylamine [2].

precipitate which formed was filtered off, and the mother liquor steamed out in vacuum. The dry residue was extracted with chloroform. After removing the solvent, 0.6 g of small colorless crystals of the lactam of β -aminoethylthioxy- ω -propionic acid separated; m.p. 109-110°; yield 55%. Found: C 45.74; H 6.75; N 10.50; S 24.90%. C_5H_9ONS . Calculated: C 45.60; H 6.90; N 10.60; S 24.50%.

Imination of tetrahydro- γ -thiopyrone*. To a freshly prepared solution of 1.6 g of hydrozoic acid and 1.9 g of tetrahydro- γ -thiopyrone in 50 g of dry chloroform was added 6.5 g concentrated sulfuric acid dropwise and with stirring. The rate of addition was such that the temperature did not go higher than 30°. The solution was then stirred until evolution of nitrogen ceased; the oily layer was separated and added dropwise to 20 g ice. The solution was neutralized to litmus with dry caustic soda, the precipitate filtered off, and the filtrate extracted with chloroform. After removing the chloroform 1.0 g of small colorless crystals of the lactam of β -aminoethylthioxy- ω -propionic acid was obtained, m.p. 109-110°; yield 50%. A mixed melt with a sample prepared by the method described above gave no depression of the melting point.

Preparation of 1,2-tetrazole- β,β' -diethylsulfide. 9.0 g of concentrated sulfuric acid was added, dropwise and with stirring, to a freshly prepared solution of 3.2 g hydrozoic acid and 1.5 g tetrahydro- γ -thiopyrone in 100 g dry chloroform at such a rate that the temperature did not exceed 30°. The reaction mixture was then stirred until evolution of nitrogen ceased; the oily layer was separated and added dropwise to ice (40 g). The solution was neutralized to litmus with 30% potassium hydroxide solution, and evaporated in a vacuum dessicator; the residue was extracted with ethanol. The alcoholic extract was evaporated and the dry residue recrystallized from hot water. 0.5 g of large rhomboidal crystals of 1,2-tetrazole- β,β' -diethylsulfide were obtained, m.p. 157°. Found: C 39.34; H 5.16; N 34.39%. $C_5H_8N_4S$. Calculated: C 39.20; H 5.25; N 34.20%.

Oxidation of the lactam of β -aminoethylthioxy- ω -propionic acid, 3 g of 30% aqueous hydrogen peroxide was added by degrees to a solution of 2 g of the lactam of β -aminoethylthioxy- ω -propionic acid at such a rate that the temperature did not exceed 40°. The solution was evaporated on a water bath in a vacuum dryer, and the residue recrystallized from absolute acid was obtained in the form of snow-white crystals with m.p. 192-193°; yield 98%. Found: C 37.02; H 5.80; N 8.44; S 19.82%. $C_5H_9O_3NS$. Calculated: C 36.80; H 5.52; N 8.58; S 19.69%.

Polymerization of the lactam of β -aminoethylthioxy- ω -propionic acid. The lactam was heated in the presence of a trace of metallic sodium (less than 1 mg per 10 g lactam) in a sealed glass tube under nitrogen for 2 hr at 180-200°. In this way a colorless glassy mass was formed, which was the polymer of the lactam of β -aminoethylthioxy- ω -propionic acid. Found: C 45.36; H 6.61; N 10.82; S 24.86%. $(C_5H_9ONS)_n$. Calculated: C 45.60; H 6.90; N 10.60; S 24.50.

Polymerization of the lactam of β -aminoethanesulfo- ω -propionic acid. In a similar way the polymer from the lactam of β -aminoethanesulfo- ω -propionic acid was prepared. Found: C 36.62; H 5.33; N 8.88; S 20.00%. $(C_5H_9O_3NS)_n$. Calculated: C 36.80; H 5.52; N 8.58; S 19.69. The polymer was soluble in concentrated nitric acid; on diluting this solution the polymer was deposited as a film.

SUMMARY

1. The lactam of β -aminoethylthioxy- ω -propionic acid was prepared by the rearrangement of tetrahydro- γ -thiopyrone oxime and by imination of tetrahydro- γ -thiopyrone.
2. Oxidation of the latter gave the lactam of β -aminoethanesulfo- ω -propionic acid.
3. Polymers were obtained from both the sulfur-containing lactams.

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* Tetrahydro- γ -thiopyrone was made by condensing bis- β -carbethoxyethylsulfide in the presence of sodium ethoxide [2].

SUCCESSIVE ELIMINATION OF THE ALCOHOL GROUPS OF 3,7-DIMETHYLOCTANE-1,7-DIOL ON A TRICALCIUM PHOSPHATE CATALYST

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pp. 2055-2056, November, 1960

Original article submitted April 20, 1960

It is known that tertiary alcohols are dehydrated most readily, while secondary alcohols lose water with more difficulty, and primary alcohols with most difficulty. It is natural to expect that tertiary, secondary, and primary alcohol groups will be eliminated from the molecule of a polyhydric alcohol in precisely this sequence. In order to check this hypothesis we investigated the dehydration of 3,7-dimethyloctane-1,7-diol. The dehydration of this diol has not been studied previously.

EXPERIMENTAL

The experiments were carried out in an apparatus of the flow type (Fig.1) at a residual pressure of 20 mm Hg. The vertical stainless steel tube 1 (25 mm in diameter) with an electrical heater 2 g was charged with 100 ml (69 g) of catalyst, which was prepared according to [1] and consisted of granules 2 x 3 mm in size. The temperature in the catalyst bed was controlled with a contact thermometer 3. The bottom of the tube was connected to an evaporator 4, which consisted of a round-bottomed flask with two side tubes, one for the thermometer 5 and the other for the dropping funnel 6. The diol dripped steadily into the flask, evaporated, and entered the reaction tube in the form of vapor. After condensation in the condenser 7, the reaction products were collected in a receiver 8 and partly in a trap 9, cooled with a mixture of ice and salt.

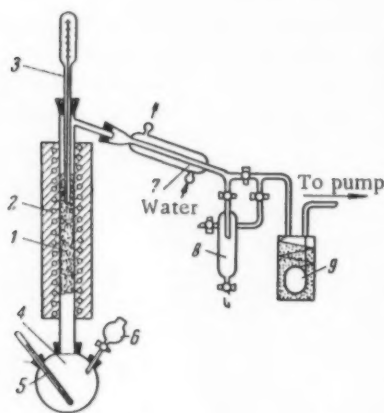


Fig.1. Plan of apparatus for dehydration in vacuum.

3,7-Dimethyloctane-1,7-diol (hydroxycitronellol) was obtained in 95% yield by hydrogenation of 3,7-dimethyloctan-7-ol-1-al (hydroxycitronellal) in alcohol over a skeletal nickel catalyst at 50° and 50-100 atm pressure. The diol had b.p. 133° (4 mm); d_4^{20} 0.9724; n_D^{20} 1.4609; found: MR 51.46; calculated MR 51.43. Literature data [2]: b.p. 124-125° (1 mm); n_D^{20} 1.4618.

In each experiment, which lasted for 15-20 min, 25-30 ml of the diol was passed. The catalyzate consisted of two layers, an aqueous one and an oily one. The latter was distilled at 22 mm to give two fractions: frac. I with b.p. 73-75° and frac. II with b.p. 128-130°, and a residue, which consisted of unreacted diol. After distillation over sodium, frac. I had the following constants: b.p. 162-164°; d_4^{20} 0.7984; n_D^{20} 1.4522. Its Raman spectrum contained two characteristic lines: 1644 cm^{-1} (1) and 1669 cm^{-1} (4).

The first indicates the presence of an α -ethylenic bond and the second, an ethylenic bond in a different position, whose determination was difficult due to the branched structure of the hydrocarbon. These properties correspond to those of 3,7-dimethyloctadiene. According to literature data [3], 3,7-dimethyloctadiene has constants which vary over the following ranges, depending on the position of the double bonds: b.p. 160-179°; d_4^{20} 0.7580-0.7933; n_D^{20} 1.4358-1.4560. After distillation, frac. II had the following constants: b.p. 128-129° (22 mm); d_4^{20} 0.8547; n_D^{20} 1.4609, which correspond to those of citronellol [3]: b.p. 118° (17 mm); d_4^{17} 0.8565; n_D^{20} 1.4566. The citronellol content of frac. II determined by bromination was 101% and by acetylation in pyridine in the cold, 89.5%.

Figure 2 shows the effect of temperature on the direction and degree of dehydration of 3,7-dimethyloctane-1,7-diol. At 200°, the diol was dehydrated selectively to citronellol, the yield of which reached 84%, and only 5% of the complete dehydration product, namely, 3,7-dimethyloctadiene, was formed. With an increase in reaction temperature, the citronellol content of the catalyzate (curve 1) fell and the yield of the diene (curve 2) increased correspondingly. At 250° the main reaction product was 3,7-dimethyloctadiene, the yield of which reached 85%, while at 290°, the yield of the latter was 90%.

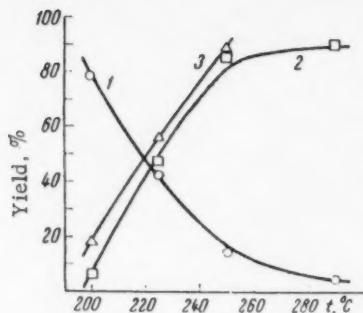
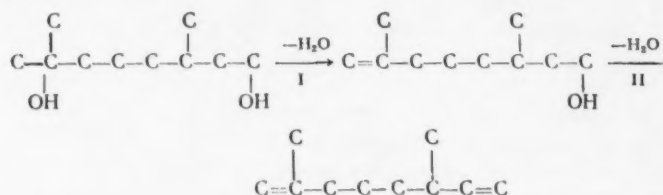


Fig. 2. Dehydration of 3,7-dimethyloctane-1,7-diol to citronellol (1) and 3,7-dimethyloctadiene (2). Dehydration of citronellol to 3,7-dimethyloctadiene (3).

of citronellol. A comparison of the data on the dehydration of 1,7-dimethyloctanediol and citronellol (curves 2 and 3) shows that 3,7-dimethyloctadiene is formed in approximately the same yield at the same temperatures. Obviously this correspondence can only occur with stepwise dehydration of the diol, when stage (II) limits the total rate of the process.

The results obtained show that the dehydration of 3,7-dimethyloctane-1,7-diol on calcium phosphate to form the diene proceeds in stages according to the scheme:



At a lower temperature, dehydration occurs only at the tertiary alcohol group and citronellol is formed, while at a higher temperature, a second water molecule is eliminated and 3,7-dimethyloctadiene is obtained. The reaction mechanism proposed was also confirmed by results obtained in the dehydration

SUMMARY

1. The dehydration of 3,7-dimethyloctane-1,7-diol on a phosphate catalyst proceeds in stages: first to citronellol and then to 3,7-dimethyloctadiene.
2. The stepwise nature of the process is caused by the position of the hydroxyl groups (primary and tertiary) in the 3,7-dimethyloctane-1,7-diol molecule.

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CONDENSATION OF GEM-DINITROALKANES WITH ALIPHATIC ALDEHYDES AND AMINES

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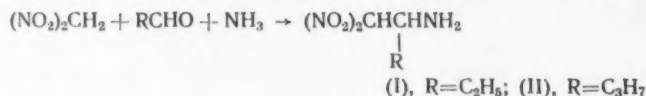
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 11,

pp. 2056-2058, November, 1960

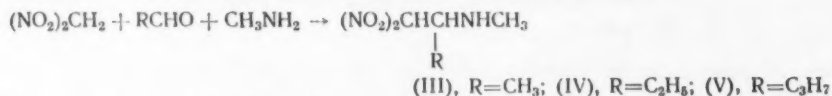
Original article submitted April 26, 1960

The Mannich reaction with nitro compounds has been studied with quite a large number of nitroalkanes and amines. As is known, formaldehyde is used as the third component in this reaction. The possibility of condensing other aldehydes with nitroalkanes and amines has not been investigated systematically up to now. In order to extend the field of application of the Mannich reaction with nitro compounds, we studied this reaction with homologs of formaldehyde, namely, acetaldehyde, propionaldehyde, and butyraldehyde. As compounds with a labile hydrogen we chose dinitromethane and its homologs, and as the amine component, ammonia and methylamine.

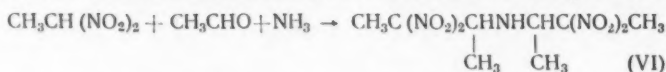
It was found that dinitromethane condenses smoothly with propionaldehyde or butyraldehyde and ammonia to give 2-amino-1,1-dinitrobutane (I) (46% yield) or 2-amino-1,1-dinitropentane (II) (46% yield), respectively:



The expected methylaminodinitroalkanes were formed smoothly when ammonia was replaced by methylamine. The yields of the reaction products, namely, 2-methylamino-1,1-dinitropropane (III), 2-methylamino-1,1-dinitrobutane (IV), and 2-methylamino-1,1-dinitropentane (V), were 77.9, 65.5, and 65.5%.

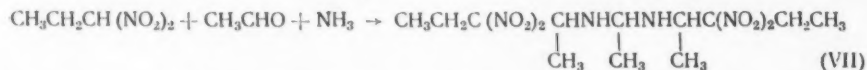


No byproducts were formed in these reactions; as a rule, the samples of aminodinitroalkanes obtained were found to be analytically pure. Like dinitromethane, 1,1-dinitroethane and 1,1-dinitropropane reacted quite readily with homologs of formaldehyde and ammonia. Thus, 1,1-dinitroethane reacted smoothly with acetaldehyde and ammonia when one molecule of ammonia condensed with two molecules of aldehyde and two molecules of dinitroethane:



The yield of 2,2,6,6-tetranitro-3,5-dimethyl-4-azaheptane (VI) was 70%.

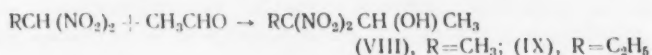
The reaction of acetaldehyde and ammonia with 1,1-dinitropropane was more complex than that with dinitroethane. The reaction product was found to be 3,3,9,9-tetranitro-4,6,8-trimethyl-5,7-diazoundecane (VII):



On the basis of our results we may conclude that the capacity to condense with homologs of formaldehyde and amines is a general property of gem-dinitroalkanes. Before the present work, the literature contained a description of only one example of a similar type, namely, the condensation of dinitromethane with acetaldehyde and ammonia [1]. Dinitromethane was the most reactive of the gem-dinitroalkanes we studied: it condensed almost instantaneously with homologs of formaldehyde and amines. The reaction may have been promoted by the fact that the products formed are internal salts; apparently, this is also the reason why the reaction products did not undergo further condensation with a second molecule of aldehyde and dinitromethane. In the case of dinitroethane, where the

condensation products do not have a salt-like nature, two molecules of aldehyde and dinitroalkane reacted with one molecule of amine. 1,1-Dinitroethane reacted more slowly than dinitromethane. 1,1-Dinitropropane reacted even more slowly, and it was the least reactive of the dinitroalkanes we studied; the yield of the condensation products was least here (21%).

In connection with the study of the condensation of gem-dinitroalkanes with aldehydes and amines, we synthesized 3,3-dinitrobutane 2-ol (VIII) and 3,3-dinitropentan-2-ol (IX):



EXPERIMENTAL

Reaction of dinitromethane with aldehydes and amines. To an ether solution of dinitromethane, obtained from 0.01 mole of its potassium salt, were added 0.01 mole of the aldehyde, 3 ml of alcohol, and 0.01 mole of 26% aqueous solution of ammonia (or 3 ml of water and 0.01 mole of 24.5% aqueous solution of methylamine) with stirring and cooling with ice water. The mixture was shaken for 15 min, cooled with ice water, and kept at normal temperature for an hour with periodic shaking. The yellow, crystalline reaction product was collected, washed with small portions of ice water and alcohol and 3-4 times with ether, and dried in air. The following compounds were obtained in this way:

2-Amino-1,1-dinitrobutane (I), yield 46%, calculated on the potassium salt of dinitromethane m.p. 117° (with decomp.). Found: C 29.43; 29.52; H 5.80; 6.10; N 25.24; 25.41%. $\text{C}_4\text{H}_9\text{O}_4\text{N}_3$. Calculated: C 29.45; H 5.56; N 25.76%.

2-Amino-1,1-dinitropentane (II), yield 46%, m.p. 112° (with decomp.). Found: C 33.84; 34.09; H 5.90; 6.17; N 23.98; 23.80%. $\text{C}_5\text{H}_{11}\text{O}_4\text{N}_3$. Calculated: C 33.90; H 6.26; N 23.72%.

2-Methylamino-1,1-dinitropropane (III), yield 77.9%, m.p. 100-101° (with decomp., in a sealed capillary, recrystallized from water). Found: C 29.57; 29.53; H 5.53; 5.57; N 25.47; 25.30%. $\text{C}_4\text{H}_9\text{O}_4\text{N}_3$. Calculated: C 29.45; H 5.56; N 25.76%.

2-Methylamino-1,1-dinitrobutane (IV), yield 65.5%, m.p. 97° (with decomp., in a sealed capillary, recrystallized from water). Found: C 34.28; 34.04; H 6.29; 6.39; N 23.94; 23.90%. $\text{C}_5\text{H}_{11}\text{O}_4\text{N}_3$. Calculated: C 33.90; H 6.26; N 23.73%.

2-Methylamino-1,1-dinitropentane (V), yield 65.5%, m.p. 82-83° (with decomp., in a sealed capillary, recrystallized from water). Found: C 37.44; 37.43; H 6.78; 6.72; N 22.19; 22.09%. $\text{C}_6\text{H}_{13}\text{O}_4\text{N}_3$. Calculated: C 37.69; H 6.85; N 21.98%.

2,2,6,6-Tetranitro-3,5-dimethyl-4-azaheptane (VI). To 0.95 ml (0.015 mole) of a 30% aqueous solution of ammonia was added a mixture of 3.6 g (0.03 mole) of 1,1-dinitroethane and 1.5 g (0.03 mole) of acetaldehyde, and the mixture shaken for 15 min with periodic cooling in ice water and left at normal temperature for two days. The precipitate was collected and washed with water and a small amount of alcohol. The yield of white, crystalline (VI) was 3.24 g (70%) and the m.p. 73-74° (recrystallized from CCl_4). Found: C 31.27; 31.46; H 4.88; 4.91; N 22.24; 22.48%. $\text{C}_8\text{H}_{15}\text{O}_8\text{N}_5$. Calculated: C 31.07; H 4.89; N 22.63%.

3,3,9,9-Tetranitro-4,6,8-trimethyl-5,7-diazaundecane (VII). To 1.45 ml (0.02 mole) of a 26% aqueous solution of ammonia was added 2 ml of water and then, with stirring and cooling, a mixture of 2.7 g (0.02 mole) of 1,1-dinitropropane and 1.65 ml (0.03 mole) of acetaldehyde. The mixture was shaken for 15 min with cooling with ice water and for 2 hr at normal temperature and then left for a day. The mixture of oil and crystals obtained was triturated with a few drops of alcohol and the reaction product collected and washed with water, the minimum amount of alcohol, and ether. The yield of yellow-green (VII) was 0.8 g (21%) and the m.p. 90°. Found: C 37.44; 37.35; H 6.42; 6.40; N 21.70; 21.73%. $\text{C}_{12}\text{H}_{24}\text{O}_8\text{N}_6$. Calculated: C 37.89; H 6.36; N 22.09%. The structure of (VII) was confirmed by determination of the number of amino groups (potentiometrically) and the molecular weight: mol. weight, found; 378 mol. weight calculated for $\text{C}_{12}\text{H}_{24}\text{O}_8\text{N}_6$, (380).

3,3-Dinitrobutan-2-ol (VIII). To a mixture of 2.4 g (0.02 mole) of 1,1-dinitroethane, 5 ml of alcohol, 1 ml of water, and 0.1 ml of 10 N NaOH was added 0.02 mole of acetaldehyde with stirring and cooling (the temperature was no higher than 30-35°). The mixture was heated for 4 days at 35-38° and neutralized with 0.1 ml of 36% HCl, the alcohol removed, the residue extracted with ether, and the extract dried with magnesium sulfate. Evaporation of the

ether left liquid (VIII). From this we obtained a 3,5-dinitrobenzoate [2] with m.p. 99-101° (recrystallized from ligroin). Found: C 36.73; 36.89; H 2.77; 2.60; N 15.44; 15.65%. $C_{11}H_9O_5N_2$. Calculated: C 36.88; H 2.81; N 15.64%.

The 3,5-dinitrobenzoate of (IX) was obtained analogously and had m.p. 143° (recrystallized from CCl_4). Found: C 38.59; 38.33; H 3.34; 3.23; N 14.79; 14.87%. $C_{12}H_{11}O_5N_2$. Calculated: C 38.71; H 3.24; N 15.05%.

SUMMARY

Gem-dinitroalkanes condense readily with acetaldehyde, propionaldehyde, butyraldehyde, and amines. The use of these aldehydes instead of formaldehyde extends the field of application of the Mannich reaction with nitro compounds.

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SYNTHESIS OF UNSATURATED ORGANOSILICON COMPOUNDS FROM PROPARGYL ALCOHOL

V. F. Mironov and N. G. Maksimova

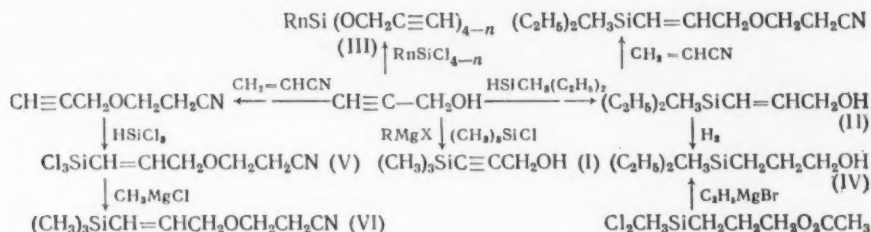
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

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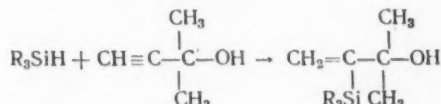
pp. 2059-2061, November, 1960

Original article submitted April 26, 1960

In the work of Petrov [1-6] and Shostakovskii [7-12] and their co-workers it was shown that there are wide possibilities of synthesizing various unsaturated organosilicon compounds from acetylenic alcohols. Dimethylethynylcarbinol and a series of its analogs and derivatives were used in these conversions. However, the possibilities of synthesizing organosilicon compounds from the simplest acetylenic alcohol, namely, propargyl alcohol, have still not been investigated. To fill this gap, in the present work we studied the series of conversions of propargyl alcohol given in the scheme below:



One should note the order of addition of R_3SiH to propargyl alcohol which we found in these conversions, and which did not correspond to the order of addition of these silanes to $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$ [2,3].



EXPERIMENTAL

γ -(Trimethylsilyl)propargyl alcohol $(\text{CH}_3)_3\text{SiC}\equiv\text{CH}_2\text{OH}$ (I). To the $\text{C}_2\text{G}_5\text{MgBr}$ from 49 g of magnesium and 230 g of ethyl bromide in 0.6 liter of ether was added 40 g of propargyl alcohol. The contents of the flask were left overnight. On the following day, 70 g of trimethylchlorosilane was added and the ether distilled from the flask. The residue was heated on a boiling water bath for 3 hr. After the addition of 400 ml of ether, the complex was decomposed with very dilute acid. The ether layer was combined with ether extracts from the aqueous layer and dried with Na_2SO_4 . After removal of the ether, vacuum distillation of the residue yielded 40 g of γ -(trimethylsilyl)propargyl alcohol with b.p. 65° (10 mm); n_D^{20} 1.4518; d_4^{20} 0.8753; found MR 39.50; calculated MR 39.48; yield 43.5%. Found: C 55.98; 56.09; H 9.34; 9.64; Si 22.29; 22.00%. $\text{C}_6\text{H}_{12}\text{SiO}$. Calculated: C 56.19; H 9.43; Si 21.90%.

Raman spectrum*. 148 (1), 173 (1 v. broad), 220 (v. broad), 261 (1), 382 (4), 438 (0), 600 (7), 645 (7), 693 (4), 763 (1), 832 (0), 975 (0), 1045 (0), 1191 (0), 1254 (4), 1404 (0), 1445 (1), 2177 (10), 2200 (8), 2959 (8).

γ -(Diethylmethylsilyl)allyl alcohol $(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiCH=CHCH}_2\text{OH}$ (II). To a mixture of 24 g of diethylmethylsilane and 16 g of propargyl alcohol was added 0.1 ml of a 0.1 N solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. Stirring formed an emulsion, which gradually disappeared on heating. Heating was stopped when the temperature of the mixture reached $140-145^\circ$. Vacuum distillation yielded 25 g of γ -(diethylmethylsilyl)allyl alcohol (II) with b.p. $99-100^\circ$ (10 mm); n_D^{20} 1.4605; d_4^{20} 0.8734; found MR 49.69; calculated MR 49.69 yield 67.5%. Found: C 60.89, 60.92; H 11.61, 11.44; Si 18.03, 18.14%. $\text{C}_8\text{H}_{18}\text{SiO}$. Calculated: C 60.69; H 11.46; Si 17.74%.

* The Raman spectra were plotted by L. A. Leites.

Raman spectrum. 245 (0), 268 (0), 403 (1 broad), 559 (5 broad), 594 (6 broad), 650 (0), 916 (0), 677 (0), 981 (2), 1019 (1), 1134 (0), 1241 (3 broad), 1305 (6 broad), 1418 (8), 1464 (9 broad), 1610 (3), 1623 (5), 2884 (10), 2909 (10), 2963 (10).

The addition product of acrylonitrile and alcohol (II) $(C_2H_5)_2CH_3SiCH=CHCH_2OCH_2CH_2CN$ was obtained in the usual way in 60% yield and had b.p. 155° (20 mm); n_D^{20} 1.4582; d_4^{20} 0.9124; found MR 63.24; Calculated MR 63.63. Found: C 62.55, 62.69; H 9.76, 9.82; Si 13.30, 12.86%. $C_{11}H_{21}SiNO$. Calculated: C 62.50; H 10.01; Si 13.28%.

γ -(Diethylmethylsilyl)propyl alcohol $(C_2H_5)_2CH_3SiCH_2CH_2CH_2OH$ (IV). Hydrogenation of 18.5 g of γ -(diethylmethylsilyl)allyl alcohol over Raney nickel in ethanol in a hydrogenation flask was continued until the theoretical amount of hydrogen had been absorbed (14 hr). Distillation yielded an alcohol with b.p. 86° (9 mm); n_D^{20} 1.4505; d_4^{20} 0.8626. Although the refractive index and boiling point of this alcohol differed somewhat from those of authentic γ -(diethylmethylsilyl)propyl alcohol [b.p. 92° (9 mm); n_D^{20} 1.4445; d_4^{20} 0.8630, obtained by the action of 5 moles of C_2H_5MgBr on $Cl_2CH_3SiCH_2CH_2CH_2O_2CCH_3$], its Raman spectrum coincided with that of authentic γ -(diethylmethylsilyl)propyl alcohol apart from very weak additional lines: 873 (1); 905 (0); 1325 (0); 2851 (1).

Raman spectrum. 550 (0), 580 (10), 597 (1), 645 (2 broad), 661 (1 broad), 710 (0), 726 (0), 752 (2 broad), 795 (0), 861 (1), 972 (3 broad), 1015 (4 broad), 1056 (2 broad), 1112 (2 broad), 1139 (2 broad), 1184 (3 broad), 1232 (3), 1251 (1), 1302 (2 broad), 1380 (1), 1415 (5 broad), 1467 (6 broad), 2875 (10), 2903 (10), 2937 (3), 2956 (10).

Propargyloxytrimethylsilane $CH \equiv CCH_2OSi(CH_3)_3$ (III). Over a period of 3 hr, 110 g of trimethylchlorosilane was added with stirring to a mixture of 56.1 g of propargyl alcohol, 79.1 g of pyridine, and 250 ml of ether. The pyridine salt formed was then removed by filtration and washed with fresh ether. After treatment with dry HCl, the filtrate was refiltered and distilled on a column. We obtained 60 g of propargyloxytrimethylsilane with b.p. 110.8° (757 mm); n_D^{20} 1.4090; d_4^{20} 0.8333; found MR 38.05; calculated MR 38.55; yield 47%. Found: C 56.19; H 9.26, 9.01; Si 21.85, 22.06%. $C_6H_{12}SiO$. Calculated: C 56.19; H 9.43; Si 21.90%.

Raman spectrum. 181 (6 broad), 217 (5 broad), 310 (5 broad), 475 (0), 614 (10 broad), 690 (1), 752 (0), 830 (0), 923 (0), 1033 (0), 1102 (0), 1185 (0), 1262 (0), 1379 (1), 1405 (1), 1452 (1), 2129 (10 broad), 2900 (10 broad), 2956 (10), 3107 (4).

The following compounds were synthesized analogously: $C_2H_5(CH_3)_2SiOCH_2C \equiv CH$: b.p. 134.8° (745 mm); n_D^{20} 1.4172; d_4^{20} 0.8339; found MR 42.92; calculated MR 43.20; $(CH_3)_2Si(OCH_2C \equiv CH)_2$: b.p. 73° (10 mm); n_D^{20} 1.4368; d_4^{20} 0.966; found MR 45.57; calculated MR 45.75; $C_2H_5Si(OCH_2C \equiv CH)_2$: b.p. 118° (10 mm); n_D^{20} 1.4550; d_4^{20} 1.0328; found MR 58.40; calculated MR 58.10.

B-(γ -Trichlorosilylallyloxy) propionitrile $Cl_3SiCH=CHCH_2OCH_2CH_2CN$ (V). A mixture of 20 g of β -propargyloxypropionitrile [b.p. 111° (15 mm); n_D^{20} 1.4450; d_4^{20} 0.9962], 32 g of trichlorosilane, and 0.5 ml of a 0.1 N solution of $H_2PtCl_6 \cdot 6H_2O$, in isopropanol was boiled for 3 hr. Vacuum distillation yielded 23 g of B-(γ -trichlorosilylallyloxy) propionitrile with b.p. 140° (7 mm); n_D^{20} 1.4780; d_4^{20} 1.2900; Found MR 53.5; calculated MR 53.67. Found: Cl 61.00; 60.89%. $C_6H_8NOCl_3Si$. Calculated: Cl 60.94%. Methylation with CH_3MgCl gave a 50% yield of B-(γ -trimethylsilylallyloxy) propionitrile (VI) with b.p. 94-96° (6 mm); n_D^{20} 1.4490; d_4^{20} 0.9084; found MR 54.13; calculated MR 54.61.

SUMMARY

γ -Trialkylsilylpropargyl and allyl alcohols, and also propargyloxysilanes were synthesized from propargyl alcohol.

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PREPARATION OF AROMATIC NITRO KETONES AND NITRO NITRILES BY THE WITTIG REACTION

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Translated from *Izvestiya Akademii Nauk SSSR*,

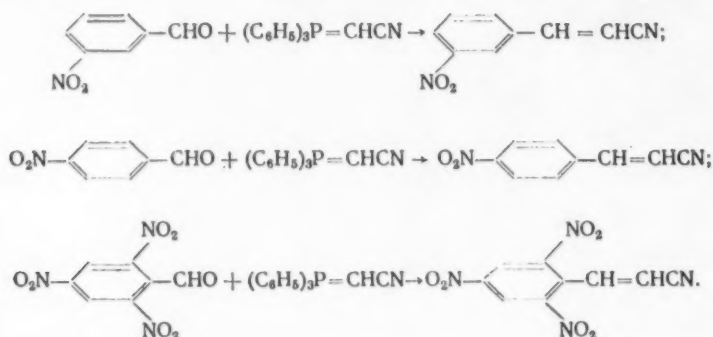
Otdelenie Khimicheskikh Nauk, No. 11,

pp. 2061-2063, November, 1960

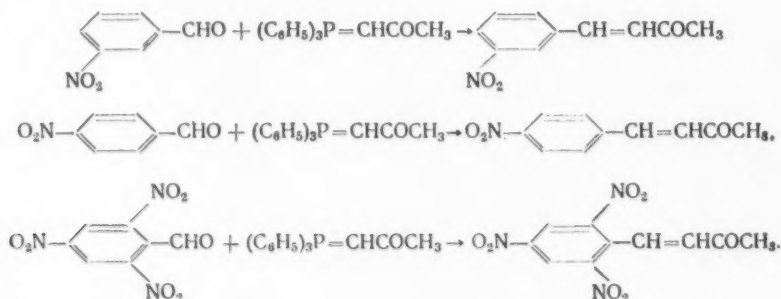
Original article submitted April 26, 1960

We recently described [1] the synthesis of methyl esters of α, β -unsaturated acids containing a nitro group by the reaction of carbomethoxymethylene-triphenylphosphine $[(C_6H_5)_3P = CHCOOCH_3]$ with appropriate aldehydes. The present work is concerned with further study of this reaction for the preparation of unsaturated aromatic nitro nitriles and nitro ketones.

Heating cyanomethylenetriphenylphosphine $(C_6H_5)_3P = CHCN$ with *m*-nitrobenzaldehyde, *p*-nitrobenzaldehyde, and *o, o'*, *p*-trinitrobenzaldehyde in benzene yielded the corresponding unsaturated nitriles:



The reaction of nitro aldehydes with acetylmethylenetriphenylphosphine $(C_6H_5)_3P = CHCOCH_3$ proceeded even more readily and gave high yields of nitrobenzalacetones:



EXPERIMENTAL

Acetylmethylenetriphenylphosphine was prepared by the method described previously [2]:



Preparation of cyanomethylenetriphenylphosphine. A mixture of 28.5 g of triphenylphosphine, 18 g of chloroacetonitrile, and 150 ml of dry benzene was boiled under reflux for 8 hr and the precipitate collected and washed with benzene to yield 36.2 g (quantitative yield) of cyanomethyltriphenylphosphonium chloride $(C_6H_5)_3PClCH_2CN$ with m.p. 244° [3]. A 24-g sample of the phosphonium salt obtained was dissolved in 550 ml of water with stirring, 50 ml of a 5% aqueous solution of sodium hydroxide gradually added with stirring, the mixture stirred for 1 hr, and the precipitate collected, washed with water, and dried in air. We obtained 18.0 g (85%) of cyanomethylenetriphenylphosphine with m.p. 188-191°. Found: C 79.75; 79.63; H 5.47; 5.55; P 10.18; 10.29%. $C_{20}H_{16}NP$. Calculated: C 79.87; H 5.33; P 10.29%.

Reaction of aldehydes with acetylmethylenetriphenylphosphine and cyanomethylenetriphenylphosphine. A mixture of equimolecular amounts of the aldehyde and the appropriate phosphorane in dry benzene was stirred for 6-10 hr at 50-60° in a stream of nitrogen, the benzene removed in vacuum, and the residue treated as described below for each particular case.

Reaction of $(C_6H_5)_3P = CHCOCH_3$ with m-nitrobenzaldehyde. The residue was extracted continuously with hot ether for 4 hr, the precipitate $[(C_6H_5)_3PO]$ removed by filtration, and the ether evaporated. We obtained m-nitrobenzalacetone in 80% yield and it had m.p. 94-95° (from alcohol). Literature data [4]: m.p. 94-95°.

Reaction of $(C_6H_5)_3P = CHCOCH_3$ with p-nitrobenzaldehyde. The residue was recrystallized from ethanol. We obtained p-nitrobenzalacetone in 92% yield and it had m.p. 109-110° (from alcohol). Literature data [5]: m.p. 110°.

Reaction of $(C_6H_5)_3P = CHCOCH_3$ with o, o', p-trinitrobenzaldehyde. The residue was extracted continuously with hot ether for 6-8 hr, when a small residue (A) remained. The ether solution deposited a precipitate (B) and the ether was removed from the solution to yield a residue (C). Fraction B was recrystallized from alcohol and fractions A and C were combined and recrystallized from alcohol; the crystals obtained were combined. We obtained o, o', p-trinitrobenzalacetone in 78% yield and it had m.p. 132-133°. Found: C 42.94; 42.97; H 2.48; 2.57; N 15.01; 15.08%. $C_{10}H_7N_3O_7$. Calculated: C 42.71; H 2.49; N 14.94%.

Reaction of $(C_6H_5)_3P = CHCN$ with m-nitrobenzaldehyde. The residue was extracted continuously with hot ether, the ether distilled from the solution, and the residue recrystallized from alcohol with a few drops of water added. We obtained the nitrile of m-nitrocinnamic acid in 72% yield; the m.p. was 160° (from alcohol). Literature data [6]: m.p. 160°.

Reaction of $(C_6H_5)_3P = CHCN$ with p-nitrobenzaldehyde. The residue was recrystallized from alcohol. We obtained the nitrile of p-nitrocinnamic acid in 74% yield; the m.p. was 202°. Literature data [6]: m.p. 202°.

Reaction of $(C_6H_5)_3P = CHCN$ with o, o', p-trinitrobenzaldehyde. The residue was washed with warm alcohol. We obtained the nitrile of o, o', p-trinitrocinnamic acid in 71% yield; the m.p. was 184-185° (from alcohol). Found: C 41.20; 41.21; H 1.49; 1.47; N 21.11; 21.40%. $C_9H_4N_4O_6$. Calculated: C 40.91; H 1.52; N 21.21%.

SUMMARY

m-Nitrobenzaldehyde, p-nitrobenzaldehyde, and o, o', p-trinitrobenzaldehyde were treated with cyanomethylenetriphenylphosphine and acetylmethylenetriphenylphosphine to yield the corresponding nitriles of cinnamic acid and benzalacetones, respectively, containing a nitro group in the benzene nucleus.

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EFFECT OF SOLUTION CONCENTRATION ON THE RADIATION YIELD OF FERROUS IRON OXIDATION AT HIGH RADIATION DOSE STRENGTHS

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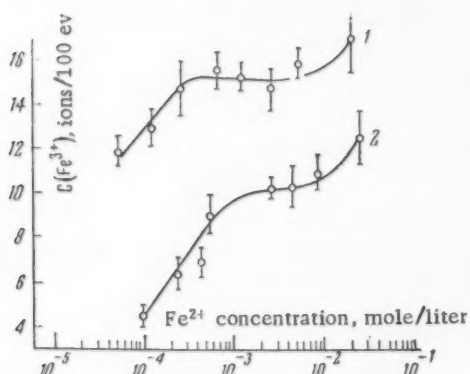
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As is known [1], the radiation yield of ferrous iron oxidation $G(\text{Fe}^{3+})$ is independent of the original solution concentration over the range of 10^{-4} - 10^{-2} mole/liter at low dose strengths. It might have been surmised that at high dose strengths the dependence of $G(\text{Fe}^{3+})$ on the original solution concentration would be more appreciable due to the high concentration of radicals in the bulk of the solution. For this purpose, we investigated the effect of high dose strengths on the value of $G(\text{Fe}^{3+})$ with solutions of Mohr's salt of various concentrations.

As in previous work [2-4], the high dose strengths were produced with pulsed electron radiation. The initial energy of the electrons equaled 0.8-0.9 Mev. The experimental procedure and measurement of the dose strength were described in our previous communication [3,4]. The solutions were irradiated in glass membranes (membrane thickness 50-60 μ). The volumes of solutions irradiated were 7-7.5 ml and the thickness of the liquid layer was 5 mm.



Relation of $G(\text{Fe}^{3+})$ to the concentration of the solution of Mohr's salt: 1) Dose strength $\sim 10^{21}$ ev/ml·sec 2) dose strength $3.5 \cdot 10^{22}$ ev/ml·sec

ble and for a $\sim 10^{-4}$ M solution, it equaled ~ 13 ions 100 ev at a dose strength of $\sim 10^{21}$ ev/ml·sec and 4.5 ions/100 ev at a dose strength of $3.5 \cdot 10^{22}$ ev/ml·sec.

Thus, an increase in the dose strength led to a decrease in the range of concentrations over which $G(\text{Fe}^{3+})$ was independent of the original solution concentration. The results obtained show that effects connected with competing reactions, namely, radical-radical and radical-solute reactions, become more appreciable at high dose strengths. It should be noted that with low concentrations of Mohr's salt and high radiation dose strengths, a considerable role is apparently played by the reaction



The occurrence of this reaction evidently leads to a decrease in the value of $G(\text{Fe}^{3+})$.

SUMMARY

The radiation yield of the oxidation of ferrous iron depends considerably on the original solution concentration at high radiation dose strengths.

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ULTRAVIOLET ABSORPTION SPECTRUM OF PYRYLIUM PERCHLORATE

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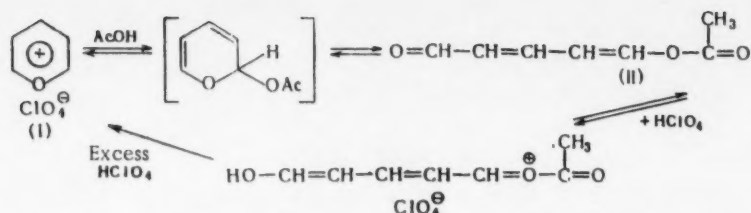
Original article submitted June 4, 1960

It has been shown [1,2] that 2,4,6-trimethylpyrylium perchlorate has two absorption bands in the near ultraviolet region: the first ("band y") at 230 m μ and the second ("band x") at 285 m μ in acetic acid or in a 0.05 N aqueous solution of perchloric acid. In connection with quantum mechanical calculations on these spectra [3], the question arose as to whether the change in extinction and the bathochromic shift observed [2] in a series of sym-trimethyl derivatives of benzene, pyridine, pyridinium, and pyrylium were caused by the heterocycle itself or by an increase in the hyperconjugation effect of the methyl groups. The spectrum of unsubstituted pyrylium perchlorate (I) was studied to solve this problem. Klagess and Trager [4] prepared substance (I) and showed that water and alcohol decompose it and that the only method of purifying it is recrystallization from 52% perchloric acid (HClO₄) at temperatures below 70°. We found that pyrylium perchlorate, which was obtained by the same method [4,5], may be recrystallized readily from anhydrous acetic acid (which did not give turbidity on dilution with carbon disulfide), containing approximately 1% of 70% perchloric acid.

TABLE Spectral Data on Six-Membered Aromatic Rings

Compound	y-band		x-band		Literature references
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	
Benzene	198	8000	255	250	[2]
Mesitylene	215	7420	265	219	[9]
Pyridine	195	7500	250	2000	[8]
Sym-collidine	прим. 216	6900	267	4000	[10]
1-Methylpyridinium perchlorate	—	—	259	4700	[11]
1,2,4,6-Tetramethylpyridinium perchlorate	221	5100	268	7340	[2,11]
Pyrylium perchlorate	219	2100	269	8800	—
2,4,6-Trimethylpyrylium perchlorate	230	4550	285	12000	[2]

Pyrylium perchlorate even withstood boiling under these conditions. However, it is so strong a Lewis acid that it reacts unselectively even with such weak nucleophilic reagents as water and alcohol, which are used as solvents in normal reactions of substituted pyrylium salts, for example, with ammonia [4], hydrogen peroxide [6], and alkali-metal cyanides [7]. Therefore, in these reactions, pyrylium perchlorate gave only indefinite solvolysis products, which were derivatives of glutaric aldehyde. The reactivity of pyrylium perchlorate is so great that its acetic acid solution rapidly decomposed filter paper. The absorption spectrum of a 10⁻⁴ M solution in anhydrous acetic acid containing 1% of 70% perchloric acid had band x with λ_{\max} 270 m μ , ϵ_{\max} 7850, and an oscillator strength $f = 0.121$. Band y did not appear due to the opacity of acetic acid below 240 m μ . A 2 · 10⁻⁴ M solution in 64% aqueous perchloric acid showed both bands with the following characteristics: y-band: λ_{\max} 219 m μ , ϵ_{\max} 2100; $f = 0.053$; λ_{\min} 237.5; ϵ_{\min} 640; x-band: λ_{\max} 269; ϵ_{\max} 8800; $f = 0.140$. The spectrum was completely different in anhydrous acetic acid in the absence of HClO₄, where there was only one intense band with λ_{\max} 304.5 m μ ; ϵ_{\max} 18,600, and $f = 0.463$, which was probably caused by the acetolysis product (II);



Spectral data for the basic 6-membered aromatic rings and the corresponding 2,4,6-trimethyl derivatives are given in the table. From the table it follows that the bathochromic effect is caused in equal measure by the heterocycle and by the substituents.

SUMMARY

The bathochromic shift observed in the ultraviolet spectra of sym-trimethyl derivatives of benzene, pyridine, pyridinium, and pyrylium is caused in equal measure by the heterocycle and by the substituents.

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LETTERS TO THE EDITOR

REACTION OF ALLYL HALIDES WITH TRICHLOROGERMANE

V. F. Mironov, N. G. Dzhurinskaya, and A. D. Petrov

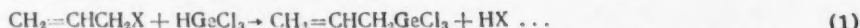
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We discovered a new reaction of trichlorogermane with allyl bromide and chloride, which leads to the formation of allyltrichlorogermane according to the equation:



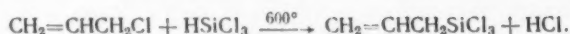
Previously, allyl trichlorogermane was obtained for the first time by direct synthesis from allyl chloride and germanium [1]. The properties, which we determined more accurately, were t_b , p. 155.5° (756 mm); n_D^{20} 1.4938; d_4^{20} 1.5480.

As is known, HGeCl_3 differs from HSiCl_3 in a higher reactivity, and with simple mixing at room temperature without catalysts, it adds at the multiple bond of various olefins and their derivatives [2,3]



However, when HGeCl_3 was added to allyl bromide, the reaction unexpectedly did not proceed according to equation (2), but according to equation (1), and allyltrichlorogermane was obtained in a yield of 37% on the allyl bromide. It was then found that when HGeCl_3 was added to allyl chloride, the reaction proceeded according to equation (1) when carried out in ether. The yield here was low (17%).

It should be pointed out that there is a similar reaction between HSiCl_3 and allyl chloride [4,5], but it occurs only at a very high temperature (600°) in the gas phase:



At the same time, the analogous reaction of HGeCl_3 with allyl chloride, which we discovered, occurred at room temperature in the liquid phase.

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NEW METHOD OF SYNTHESIZING AROMATIC COMPOUNDS OF GERMANIUM

L. I. Emel'yanova and L. G. Makarova

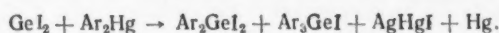
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We showed that the reaction of a diarylmercury with salts of divalent germanium leads to more highly arylated compounds of germanium than arylation of germanium tetrachloride with a diarylmercury [1], which gives only mono-arylgermanium compounds. Boiling equimolecular amounts of the diarylmercury and germanium diiodide in toluene for 15 min gave a high yield of di- and triaryl organogermanium compounds. The reaction scheme was as follows:



The experimental results are given in the table.

TABLE Organogermanium Compounds Prepared

Formula	M.p., °C	Yield, %	Formula	M.p., °C	Yield, %
(C ₆ H ₅) ₂ GeI ₂	62—64	69	(<i>m</i> -ClC ₆ H ₄) ₂ GeI ₂	61—63	73
(C ₆ H ₅) ₃ GeI	152—154	25,7	(<i>o</i> -BrC ₆ H ₄) ₂ GeI ₂	155,5—	68
(<i>p</i> -CH ₃ C ₆ H ₄) ₂ GeO	221,5—	63,7		157,5	64
	222,5		(<i>p</i> -BrC ₆ H ₄) ₃ GeI	170—171	28
(<i>o</i> -CH ₃ C ₆ H ₄) ₂ GeI ₂	85—86,5	45,7	(<i>p</i> -BrC ₆ H ₄) ₃ GeO		80
(<i>m</i> -CH ₃ C ₆ H ₄) ₂ GeI	76—77,5	60	(<i>p</i> -CH ₃ OC ₆ H ₄) ₃ GeI	114—115	53,5
(<i>p</i> -ClC ₆ H ₄) ₂ GeI ₂	67,5—69	74	(<i>p</i> -C ₂ H ₅ OC ₆ H ₄) ₃ GeI	95,5—97	62
(<i>p</i> -ClC ₆ H ₄) ₂ GeI	133—134	7	(<i>o</i> -C ₂ H ₅ OC ₆ H ₄) ₂ GeI ₂	137—138	50
(<i>o</i> -ClC ₆ H ₄) ₂ GeI ₂	124—	33,7	(β-C ₁₀ H ₇) ₂ GeI	174—176	14,7
	125,5		(β-C ₁₀ H ₇) ₂ GeO	211—	
				212,5	

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ACTION OF ETHYL MERCAPTAN ON TRIALLYLBORON

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, No. 11,

p. 2068, November, 1960

Original article submitted August 10, 1960

We found that triallylboron reacts with ethyl mercaptan at -15° , and with equimolecular amounts of the reagents we obtained propylene and the ethyl ester of diallylthioboric acid in 62.5% of theoretical yield; b.p. $67-70^{\circ}$ (11 mm); d_4^{20} 0.8419; n_D^{20} 1.4719. Found: C 62.70; H 10.05; B 6.86%; MR 51.24. $C_8H_{15}BS$. Calculated: C 62.36; H 9.81; B 7.02%; MR 51.28.

The action of 2 moles of ethyl mercaptan on 1 mole of triallylboron formed: 1) the diethyl ester of allylthioboric acid in 51.8% of theoretical yield; b.p. $62-64^{\circ}$ (2 mm); d_4^{20} 0.9563; n_D^{20} 1.5182. Found: C 48.60; H 8.66; B 6.39%; MR 55.20. $C_7H_{15}BS_2$. Calculated: C 48.28; H 8.68; B 6.21%; MR 55.76. 2) the product from the addition of ethyl mercaptan to the double bond of the diethyl ester of allylthioboric acid in 31.8% of theoretical yield; b.p. $133.5-134^{\circ}$ (2 mm); d_4^{20} 1.0076; n_D^{20} 1.5312. Found: C 45.97; H 8.91; B 4.58%; MR 72.57. $C_9H_{21}BS_2$. Calculated: C 45.75; H 8.96; B 4.58%; MR 73.47.

We established that the latter compound may be obtained in 77.4% of theoretical yield by mixing ethyl mercaptan with the diethyl ester of allylthioboric acid. Ethyl mercaptan is also capable of adding to the di-n-butyl ester of allylthioboric acid to form the di-n-butyl ester of 2-ethylmercapto-n-propylboric acid with b.p. $104-106^{\circ}$ (1.5 mm); d_4^{20} 0.9035; n_D^{20} 1.4514.

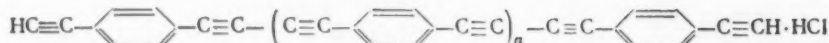
Found: C 60.22; H 11.18; B 4.20%; MR 77.62. $C_{13}H_{29}BO_2S$.

Calculated: C 59.99; H 11.23; B 4.16%; MR 77.44.

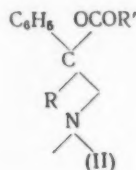
CORRECTIONS

In No. 5 (1960) p. 811, the expression in the third column of the table should read: $[k \cdot 10^{13}]$ in $\text{cc} \cdot \text{sec}^{-1}$.

On p. 951 the first formula from the top should read:



In No. 10 on p. 1821 formula (II) should read:



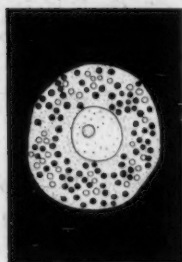
Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN
				Vol. Issue Year
AE	Atomnaya energiya	Soviet Journal of Atomic Energy	Consultants Bureau	1 1 1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics - Acoustics	American Institute of Physics	1 1 1955
Astr.(on). zh(urn).	Antibiotiki	Antibiotics	Consultants Bureau	4 1 1959
Avto(mat). svarka	Astronomicheskiy zhurnal	Soviet Astronomy—AJ	American Institute of Physics	34 1 1957
	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)	
	Avtomatika i Telemekhanika	Automatic and Remote Control	Instrument Society of America	1 1959
	Biofizika	Biophysics	National Institutes of Health*	27 1 1956
	Biohimiya	Biochemistry	Consultants Bureau	21 1 1955
	Byulleten' eksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41 1 1959
DAN (SSSR)				
Doklady AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:	American Institute of Biological Sciences	106 1 1956
		Doklady Biochemistry Section	American Institute of Biological Sciences	112 1 1957
		Doklady Biological Sciences Sections (includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)		
		Doklady Botanical Sciences Sections (includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112 1 1957
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112 1 1957
		Doklady Earth Sciences Sections (includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124 1 1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106- 1 1957- 6 1958
		Proceedings of the Academy of Sciences of the USSR, Section: Geology	Consultants Bureau	106- 1 1957- 6 1958
		Doklady Soviet Mathematics	The American Mathematics Society	131 1 1961
		Soviet Physics—Doklady (includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)		
		Wood Processing Industry	American Institute of Physics	106 1 1956
		Telecommunications	Consultants Bureau	106- 1 1956- 117 1957
		Entomological Review	Timber Development Association (London)	9 1959
		Pharmacology and Toxicology	Massachusetts Institute of Technology*	1 1957
		Physics of Metals and Metallography	American Institute of Biological Sciences	38 1 1959
		Schenov Physiological Journal USSR	Consultants Bureau	20 1 1957
		Plant Physiology	Acta Metallurgica*	5 1 1957
		Geochemistry	National Institutes of Health*	1 1957
		Soviet Physics—Solid State Measurement Techniques	American Institute of Biological Sciences	4 1 1957
		Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	The Geochemical Society	1 1958
			American Institute of Physics	1 1959
			Instrument Society of America	1 1959
			Consultants Bureau	1 1952
Derevobrabat. prom-st'.				
	Derevobratyayushchaya promyshlennost'			
	Élektrosvyaz			
	Entomologicheskoe obozrenie			
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	Fizika metallov i metallovedenie			
	Fiziologicheskii zhurnal im. I. M. Sechenova			
	Fiziologiya rastenii			
	Geokhimiya			
	Fizika tverdogo tela			
	Izmeritel'naya tekhnika			
	Izvestiya Akademii Nauk SSSR, Otdelenie khimicheskikh nauk			
Éntom(ol). oboz(renie)				
Farmakol. (i) toksikologiya				
FMM				
Fiziol. zhurn. SSSR (im. Sechenova)				
Fiziologiya rast.				
FTT				
Izmerit. tekhnika				
Izv. AN SSSR, Otd. Kh(im). N(auk)				

continued

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Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: fizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	1	1958
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Soviet Rubber Technology	18	1959
Kauch. i rez.	Kauchuk i rezina	Kinetics and Catalysis	1	1960
	Kinetika i kataliz	Coke and Chemistry USSR	1	1958
	Koks i khimiya	Colloid Journal	14	1952
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Soviet Physics - Crystallography	2	1957
Metalov. i term. obrabot. metal.	Kristallografiya	Metal Science and Heat Treatment of Metals	6	1958
	Metallovedenie i termicheskaya obrabotka metallov	Metallurgist	1	1957
Met. i top. Mikrobiol. OS	Metallurgiya i topliva	Russian Metallurgy and Fuels	26	1960
	Mikrobiologiya	Microbiology	1	1957
	Optika i spektroskopiya	Optics and Spectroscopy	6	1959
	Pochvovedenie	Soviet Soil Science	1	1958
	Priroboostroyeniye	Instrument Construction	1	1959
Priboiy i tekhn. eksperimenta	Priboiy i tekhnika eksperimenta	Instruments and Experimental Techniques	1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	1	1958
PTÉ	(see Priboiy i tekhn. éks.)	Problems of the North	1	1957
Radioelektr. Radiotekh. i élektronika	Problemy Severa	Radio Engineering	12	1957
	Radioelekhnika	Radio Engineering and Electronics	2	1957
	Stanki i instrument	Machines and Tooling	1	1959
Stek. i keram.	Steklo i keramika	Stal (in English)	1	1959
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Glass and Ceramics	13	1956
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primeneniye	Welding Production	4	1959
	Tsvetnyye metally	Theory of Probability and Its Applications	1	1956
Tsvet. Metalliy	Uspekhi fizicheskikh Nauk	Nonferrous Metals	1	1956
UFN	Uspekhi khimii	Soviet Physics - Uspekhi (partial translation)	1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Chemical Reviews	66	1958
Usp. fiz. nauk	(see UFN)	Russian Mathematical Surveys	15	1960
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Usp. matem. nauk	(see UFN)			
Usp. sovr. biol.	Voprosy sovremennoi biologii	Russian Review of Biology	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i pereivaniya krovi	Problems of Hematology and Blood Transfusion	1	1957
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ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	7	1952
ZhETF	Zhurnal éksperimental'noi i teoreticheskoi fiziki	Soviet Physics-JETP	28	1955
Zh. éksperim. i teor. fiz.	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	7	1959
ZhFZh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Journal of Microbiology, Epidemiology and Immunobiology	1	1957
ZhMEI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii			
ZhNKh	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	1	1959
Zh(urn). neorgan(ich). khim(ii)				
ZhOKh	Zhurnal obshchei khimii	Journal of General Chemistry USSR	19	1949
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ZhPKh	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	23	1950
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ZhSKh	Zhurnal struktural'noi khimii	Journal of Structural Chemistry	1	1960
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ZhTF	Zhurnal tekhnicheskoi fiziki	Soviet Physics-Technical Physics	26	1956
Zh(urn). tekhn. fiz.				
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshego nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	1	1958

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ACHIEVEMENTS IN SOVIET MICROBIOLOGY

Edited by A. A. Imshenetskii

Director of the Institute of Microbiology
of the Academy of Sciences of the USSR

TRANSLATED FROM RUSSIAN

(Original published for the Institute
of Microbiology,
Academy of Sciences of the USSR,
by the Academy of Sciences Press,
Moscow)

This concise survey of recent developments in (as well as projected directions of) Soviet microbiology is divided into four major sections:

- I. Progress in General Microbiology, *A. A. Imshenetskii*
A broad review which enables the Western scientist to see clearly the direction in which Soviet microbiologists are making their studies.
- II. Achievements of Soviet Microbiology in the Field of the Study of the Geological Activity of Microorganisms, *S. I. Kuznetsov*

In a field which has not been widely considered by Western scientists, this paper indicates great advances made in the USSR. The use of microorganisms in petroleum research and recovery are discussed, as are Soviet efforts to classify precisely and map out geologic or ecologic microbiological strata as they occur in the geologist's scheme. This article summarizes Soviet research into the relationships of various groups of microorganisms to geological — petroleum — inorganic substrates environments.

- III. Forty Years of Technical Microbiology in the USSR, *V. N. Shaposhnikov, N. D. Ierusalimskii, and I. L. Rabotnova*

Noteworthy in this paper (which deals with fermentation microbiology, acetone-butanol, organic acids, riboflavin, antibiotics, etc.) is Shaposhnikov's description of disagreement in the USSR, as there has been in the West, on the biosynthesis of citric acid by various species of *Aspergillus*.

- IV. Achievements in the Field of Soil Microbiology in the USSR, *E. N. Mishustin*

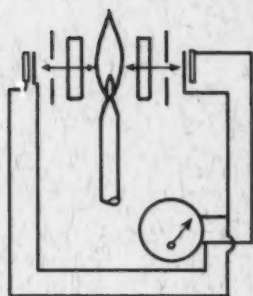
Soviet research in this area places particular emphasis on rhizosphere, root nodule, and nitrogen-fixing bacteria, and on the relationship between higher plants and associated microorganisms. Special attention is given to Vinogradskii's early description of auxotrophs and Krasilnikov's recent classification of actinomycetous microorganisms. Some comment is made on methodology, especially microbial counts and selection techniques.

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by N. S. Poluëktov

TRANSLATED FROM RUSSIAN

Original published by the
State Scientific-Technical Press
for Chemical Literature, Moscow

This volume contains a practical and comprehensive survey of the techniques employed and the instruments required for this important rapid analysis method, as well as a brief account of the theoretical principles involved. Experimental procedures and the design of apparatus are discussed at length, making the relevant chapters a valuable manual for all chemists concerned with analytical problems.

The second half of the book deals with the determination of individual elements in a variety of materials, providing much factual information, together with a complete and international bibliography. There are many useful tables, and two appendices which consider wavelengths of brightest spectral lines and peaks of molecular bands of elements excited in flame, and recommended wavelengths of spectral lines and peaks of molecular bands for determination of elements with the aid of a spectrophotometer employing glass optics and using an air-acetylene flame.

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